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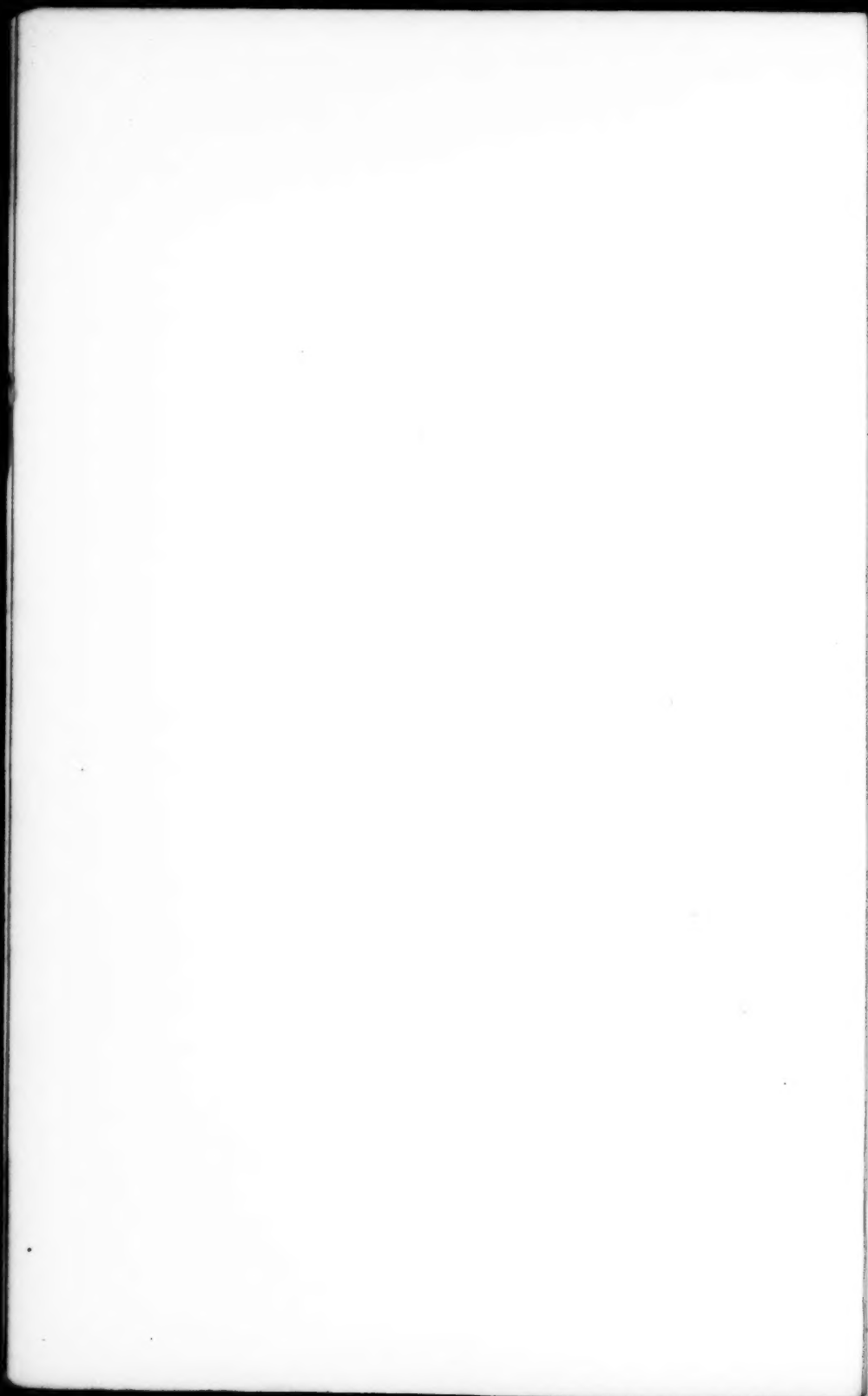
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ERRATUM.

Page 56, line 31, *for* My friend Dr. Wollaston's relative *read* My friend Mr. Howard's relative.



THE  
QUARTERLY JOURNAL  
OF THE  
CHEMICAL SOCIETY.

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Dec. 3, 1849.

The PRESIDENT in the Chair.

A Paper: "On the composition and money-value of different varieties of Guano, by J. T. Way," was presented by the Author.

The following Papers were read:

"Researches on the Volatile Organic Bases," Part VII, by Dr. Hofmann, (Vol. II. p. 300).

I.—*Analysis of Deep Well-water, from Messrs. Holt's Brewery, Ratcliffe.*

*By* JOHN MITCHELL, F.C.S.

The water forming the subject of the present communication was obtained from a well sunk on the premises of Messrs. Holt, the brewers, of Ratcliffe. The entire depth of the well in question is about 215 feet. At the depth of 165 feet, an abundance of water poured in from the sand; this, however, was kept out by means of iron tubing, and the boring continued into the chalk for 50 feet, making the entire depth 215 feet. The bore-hole in the chalk was left plain. The water rises to within 40 feet of the surface.

The specific gravity of the water is 1000·894, distilled water being 1000. It has an alkaline reaction. Qualitative analysis pointed out the presence of lime, magnesia, potash, soda, sulphuric

acid, chlorine, silicic acid, carbonic acid, organic matter, and traces of phosphoric acid; and quantitative analysis gave the following numbers :

Determination of total amount of fixed constituents.

Amount of water.	Fixed residue.	Percentage.
5400 grs.	2.7 grs.	.05000
10000 „	5.104 „	.05104
		<hr/>
Mean		.05052

Determination of sulphuric acid.

Amount of water.	Amount of BaO, SO <sub>3</sub> .	Percentage of SO <sub>3</sub> .
7200 grs.	1.27 grs.	.0060607
10000 „	1.764 „	.0060620
		<hr/>
Mean		.00606135

Determination of chlorine.

Amount of water.	Amount of Ag Cl.	Percentage of Cl.
3600 grs.	1.27 grs.	.0087207
10000 „	3.526 „	.0087162
		<hr/>
Mean		.00871845

Determination of silicic acid.

Amount of water.	Amount of Si O <sub>2</sub> .	Percentage of Si O <sub>2</sub> .
10400 grs.	.170 grs.	.0016346
10000 „	.164 „	.0016400
		<hr/>
Mean		.0016373

Determination of lime.

Amount of water.	Amount of CaO, CO <sub>2</sub> .	Percentage of CaO.
10400 grs.	1.07 grs.	.0057615
10000 „	1.03 „	.0057681
		<hr/>
Mean		.00576475

Determination of magnesia.

Amount of water.	Amount of 2 (MgO), PO <sub>5</sub> .	Percentage of MgO.
10400 grs.	4.266 grs.	.0015027
10000 „	4.102 „	.0015026
		<hr/>
Mean		.00150265

## Determination of the alkalis.

Amount of water.	Amount of mixed chlorides.	Percentage of mixed chlorides.
10000 grs.	3·34 grs.	·0334
10000 „	3·351 „	·03351
		Mean ·033455

## Determination of potash.

Amount of water.	Amount of Pt Cl <sub>2</sub> , K Cl.	Percentage of KO.
10000 grs.	·500 gr.	·00096483
10000 „	·511 „	·00098571
		Mean ·00097527

## Determination of soda.

Amount of water.	Amount of Na Cl.	Percentage of NaO.
10000 grs.	3·187293 grs.	·01689587
10000 „	3·195000 „	·01693350
		Mean ·01691478

## Determination of carbonic acid.

30,000 grs. of water, treated with a mixture of chloride of calcium and ammonia, furnished a precipitate weighing 18·33 grs. The carbonic acid contained in this was as below.

Amount of precipitate.	Amount of CO <sub>2</sub> .	Percentage in precipitate.
18·33 grs.	5·000 grs.	27·277

The above quantity of carbonic acid represents a percentage in the ratio of ·01666.

## Determination of organic matter.

140,000 grs. of water were evaporated down to a few ounces; the precipitate (*a*) collected on a filter, amounted to 20·4 grs., and the amount of water (*b*) with washings, was 5300 grs. Both the precipitate and the liquid were carefully examined for phosphoric acid, and the result shewed that both contained but inappreciable quantities.

2650 grs. of the liquid (*b*) were evaporated to dryness with carbonate of soda, and the filtered solution, on the addition of water, evaporated to dryness and weighed; it was then ignited and again weighed; it had lost ·574 gr. = ·00082 per cent of organic matter in the water.

From the above results, the following composition is deduced, shewing the amount of substances found by analysis, without regard to their state of combination :

	Grs. per Imperial Gallon.
Sulphuric acid . . . .	4·242945
Chlorine . . . .	6·102915
Silicic acid . . . .	1·146110
Lime . . . .	4·045315
Magnesia . . . .	1·051855
Potash . . . .	·682689
Soda . . . .	11·840346
Sesquioxide of iron . .	·133805
Organic matter . . . .	·574000
Combined carbonic acid .	6·982483
	<hr/>
	36·802463

Amount of solid matter per gallon, calculated as combined :

	Grs. in Imperial Gallon.
Carbonate of lime . . . .	7·223776
Carbonate of magnesia . .	2·174105
Carbonate of iron . . . .	·194074
Carbonate of soda . . . .	6·280179
Sulphate of soda . . . .	6·499744
Chloride of sodium . . . .	10·057509
Sulphate of potash . . . .	1·262068
Silicic acid . . . .	1·146110
Organic matter . . . .	·574000
	<hr/>
	35·411565*

Making the numbers in both cases in the gallon alike. The amount of solid substance found by direct experiment was 35·36 grs. per gallon, by analysis 35·411895 grs.

The amount of potash is small in comparison with that found by Messrs. Abel and Rowney in the Trafalgar Square water, and therefore corresponds better with the amounts found by Professors Graham and Brande.

\* The oxygen being deducted from the soda estimated as such, causes the difference between the actual and calculated results. This being added, would give the same amount as above.

Dec. 17, 1849.

The PRESIDENT in the Chair.

The following presents were announced :

"The Pharmaceutical Journal," for December, from the Editor.

"The Journal of the Franklin Institute," for October, from the Institute.

A. Völker, Ph. D. was duly elected a Fellow of the Society.

The following Papers were read :

"On Titanium," by Professor Wöhler, (Vol. II. p. 352).

II.—*On the Action of Sulphur upon the Pentachloride of Phosphorus.*

By J. H. GLADSTONE, PH. D. F.C.S.

The object of the present communication is to describe a substance, which was first noticed by me during my researches upon the compounds of the halogens with phosphorus, but, on account of its very distinct character, was reserved for separate consideration. I found, that when sulphur and pentachloride of phosphorus are mixed together, and heat applied, combination takes place; a mass of colourless crystals is formed, which, if the heat be continued, are converted into a yellow liquid, that may be distilled, and obtained pure by repeating the distillation. This liquid contains phosphorus, chlorine, and sulphur, but differs from the sulphochlorides of phosphorus already known, both in physical and chemical properties. Attempts to analyze the new substance, by oxidizing it with nitric acid, failed, because the heat evolved during the reaction volatilized part of the liquid. The results, however, appeared to indicate that the sulphur and phosphorus were in the proportion of 4 to 1; and this led me to the best method of preparing the compound, which is as follows.

Three parts of pentachloride of phosphorus are mixed in a small retort with 1 part of sulphur; that is, 1 equiv. of the former to rather more than 4 equivs. of the latter, and combination is deter-

mined by heating the mixture till it begins to fuse. There are then formed in the retort a yellow liquid, and a mass of transparent, colourless crystals, differing in appearance from the pentachloride of phosphorus. A gentle heat must be maintained until this transformation has taken place throughout the whole mass, when the crystalline body will be found gradually to disappear, and the liquid to increase in quantity. On cooling, the crystals are reproduced; but if the liquid be briskly boiled, a distillate will be obtained, from which only a small quantity of crystals separates. A transformation has thus been effected; for the whole liquid may be distilled over, the thermometer, which at first indicated about  $110^{\circ}$  C. ( $230^{\circ}$  F.) gradually rising; and nothing remains in the retort, except perhaps a small quantity of a peculiar dark-coloured viscid matter, which will be immediately described.

If a smaller proportion of sulphur be employed, the same products result; but unaltered pentachloride of phosphorus is found in the retort after distillation.

If, on the contrary, a larger proportion of sulphur be mixed with the pentachloride of phosphorus, both substances are likewise produced; but, during the distillation of the yellow liquid, it assumes a deep colour, and there remains in the retort a dark brown mass. This is a mixture of sulphur with another substance, which may be distilled by the heat of a spirit-lamp. It is of a viscid consistence; water has no effect upon it, but alkalis appear to separate some chlorine. I believe it to be a secondary product, resulting from the action of sulphur upon the new liquid itself at an elevated temperature.

Under no circumstances have I remarked the least trace of dichloride of sulphur, free chlorine, or any other product accompanying the reaction just described. The crystalline and the liquid body are found in various proportions, and sometimes there remains scarcely any amount of crystals. Thus it would appear, that the liquid at least is formed by the direct combination of sulphur with the pentachloride of phosphorus.

#### LIQUID COMPOUND.

No method of rectifying the liquid compound with perfect accuracy has presented itself to me. The crystalline body will rise in vapour along with it; but an approximate separation may be effected by decanting the liquid from the crystals, and submitting it to gentle



distillation. That which passes over first must be redistilled until a product is obtained, which boils uniformly at a temperature not exceeding  $125^{\circ}$  C. ( $257^{\circ}$  F.).

The substance thus prepared is a clear mobile liquid, of rather high refracting power, heavier than water, of a pale yellow colour, and possessing an odour somewhat acid, but not powerful. It evaporates at ordinary temperatures, and shows great disposition to rise in vapour, when heated. This and other causes have combined to prevent my determining its boiling point within a degree or two, but it is about  $118^{\circ}$  C. ( $244.4^{\circ}$  F.). It showed no disposition to fuse when immersed in a mixture of ice and common salt, at a temperature of  $-17^{\circ}$  C. ( $1.4^{\circ}$  F.). It is capable of dissolving a large amount of sulphur when hot, which it deposits again in crystals of the form of rhomboidal octohedrons, or sometimes in needles. It also dissolves phosphorus, almost to an unlimited extent when hot, and deposits that substance also on cooling in a crystalline form. The same may be said of the pentachloride of phosphorus. The new liquid under consideration dissolves iodine, imparting a deep red colour to the solution, as is the case with most of these liquid compounds of phosphorus and the halogens. It mixes with bisulphide of carbon. Strong sulphuric acid has no action upon it, at least in the cold; and instead of dissolving in ether, alcohol, or oil of turpentine, it violently attacks these organic solvents.

The new liquid is not affected by hydrogen gas, either at the ordinary or boiling temperature; but if a stream of hydrosulphuric acid be passed over it, sulphur separates, bubbles of gas rise through the liquid, and another liquid compound remains. Metals decompose the substance under consideration, in some cases with, in other cases without the assistance of heat. It is violently oxidized by nitric acid. When it is brought into contact with water, decomposition instantly commences; the characteristic odour of sulphochloride of phosphorus is perceptible; and after a few hours, there remains a quantity of sulphur, contaminated with some sulphide of phosphorus, and in solution, hydrochloric, sulphuric, phosphoric, and perhaps phosphorous acid, together with another acid containing both phosphorus and sulphur, and giving a brown precipitate with nitrate of silver, not soluble in dilute nitric acid, but slightly so in ammonia. I believe this to be the sulphoxyphosphoric acid described by Wurtz,\* notwithstanding the remark of that chemist, that the silver-salt is

\* Ann. Chim. Phys. [3], XX, 372.

too unstable to be prepared. The same decomposition results, only more rapidly, when solutions of the alkalis are employed; in that case, however, the liquid, before being entirely destroyed, assumes a dark red colour, and the sulphur which separates is mixed at first with flocculent masses, of an orange tint. A remarkable circumstance attending this reaction is the total absence of hydrosulphuric acid among the numerous resulting compounds, unless the solution be boiled, in which case it probably arises from decomposition of the sulphoxyphosphoric acid.

It appeared to me that this decomposition by water might be taken advantage of for the ultimate analysis of the compound, provided means could be devised for completely separating the phosphorus, sulphur, and chlorine existing under so many different forms. The following process I found effectual:—The liquid, having been weighed, was decomposed by a dilute solution of ammonia, in a corked flask, so as to prevent loss of the liquid by evaporation. When the decomposition was complete, nitrate of silver was added, which produced a dark brown precipitate, and rendered the ammoniacal solution of an inky appearance. This was boiled briskly for some minutes, until the precipitate completely separated, leaving a clear supernatant liquid. The black precipitate was then collected, well washed with ammonia, and afterwards oxidized by means of strong nitric acid. If pure sulphur separated, it was collected by itself. The nitric acid solution thus obtained was added to the previous ammoniacal solution; the chloride of silver was recovered by completely acidifying the liquid by additional nitric acid if necessary, and the sulphuric and phosphoric acids were estimated by baryta. It was found necessary to continue the boiling of the ammoniacal solution for several minutes, or the whole amount of chlorine was not converted into silver-salt.

I. 0.3765 grm. of the new liquid yielded 0.988 grm. of chloride of silver, 0.059 grm. of free sulphur, 0.222 grm. of sulphate of baryta, and 0.1047 grm. of phosphoric acid.

II. 0.1882 grm. of a separate preparation yielded 0.253 grm. of sulphate of baryta, and 0.0494 grm. of phosphoric acid, besides 0.010 grm. of free sulphur.

III. 0.788 grm. of a separate preparation, having a somewhat higher boiling-point, yielded 2.041 grms. of chloride of silver, 1.001 of sulphate of baryta, and 0.068 grm. of phosphoric acid, besides 0.130 grm. of free sulphur, which proved, however, to contain phosphorus.

IV. 0.254 grm. of the new liquid was analyzed in a totally different manner. It was poured into a flask containing reduced copper, which was corked up until the odour of the liquid had entirely disappeared. The resulting mass was exhausted with hot water, and afterwards oxidized by nitric acid. Owing to the formation, I imagine, of dichloride of copper, the chlorine was in a great measure contained in that portion which was subjected to the action of nitric acid; hence an almost inevitable loss. However, it yielded 0.6265 grm. of chloride of silver, equivalent to 60.84 per cent of chlorine. The sulphate of baryta obtained was 0.451 grm.

V. 0.4175 grm. was analyzed in the same manner as the last, iron being employed in place of copper. The application of heat was necessary to effect the decomposition. 0.521 grm. of sulphate of baryta was obtained, and 0.031 grm. of free sulphur.

These results reckoned to 100 parts are:

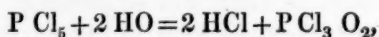
	I.	II.	III.	IV.	V.
Phosphorus . . .	12.3	11.7	{ 37.8 }	—	—
Sulphur . . . .	23.8	23.8		24.5	24.6
Chlorine . . . .	64.7	—		—	—

These numbers accord sufficiently with these deduced from the formula  $PS_4 Cl_5$ .

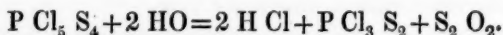
Phosphorus . . . .	11.70
Sulphur . . . . .	23.40
Chlorine . . . . .	64.90
	<hr/>
	100.00

Several views may be taken of the rational constitution of this new liquid compound. It may be considered as a double chloride of phosphorus and sulphur; thus,  $P Cl_3, 2 (S_2 Cl)$ ; but the action of water upon the substance appears to assimilate it to those compounds in which phosphorus is combined with five atoms of halogen, two of them being easily replaceable by sulphur or oxygen. We may regard it, therefore, as  $P Cl_3 S_2, 2 (S Cl)$ , and suppose the sulphochloride set free by the decomposition of the chloride of sulphur;—or as pentachloride of phosphorus in direct combination with four atoms of sulphur;  $P Cl_5 S_4$ . This is the view I prefer, and I shall accordingly designate the new liquid as sulpho-perchloride of phosphorus. The manner in which water acts upon this compound will then appear

analogous to its mode of action upon the pentachloride of phosphorus itself; that is, two atoms of hydrogen remove two of the five atoms of chlorine; but the two atoms of oxygen thus liberated, instead of entering into the composition of the new substance, combine in this case with two of the atoms of sulphur, leaving the other two still to form part of the phosphorus compound.



and



The existence of hyposulphurous acid in the solution is hypothetical; and I must remark that, where a considerable amount of water was employed, I never observed sulphurous acid among the products, even when the decomposition was effected by means of dilute acid. But, unless in large quantity, the odour would be masked by that of the sulphochloride, and there are many conceivable ways in which the sulphurous acid might be immediately reduced or oxidized. Yet, upon adding a very small quantity of water to a portion of the liquid in a corked tube, a strong pungent odour was observed when the cork was removed, and the gas produced a blue colour when suffered to fall upon a mixture of starch and solution of iodate of potash. We may, therefore, conclude that sulphurous acid was evolved.

I may here observe that sulphochloride of phosphorus, prepared in the manner described by Serullas, and decomposed by water or solutions of alkalis, without the aid of heat, gives the acid formerly referred to, which yields a brown silver-salt, and not a trace of hydrosulphuric acid.

The view which regards the liquid just examined as a direct compound of sulphur with the pentachloride of phosphorus, receives additional support from the discovery of Kremers, who has recently shown\* that sulphurous acid combines directly with pentachloride of phosphorus, giving rise to two liquids, each resolvable by water into sulphurous acid, with phosphoric and hydrochloric acids. These he terms sulphites of the pentachloride of phosphorus, with the formulæ  $\text{P Cl}_5, 2 \text{SO}_2$ , and  $\text{P Cl}_5, 3 \text{SO}_2$ . Rose's sulphate of the pentachloride of phosphorus is a substance about which too little is accurately known to warrant us in drawing any deductions from it.

\* Ann. Ch. Pharm. June, 1849.

In order to ascertain whether another compound, of different formula, could be obtained from the liquid under examination, by merely collecting that which rose first in vapour, I subjected a portion for some time to a temperature not exceeding  $100^{\circ}$  C. The portion which evaporated, condensed into a clear yellow liquid, apparently identical with that formerly examined. 0.385 grm. analyzed as above, yielded 1.020 grms. of chloride of silver; the estimation of sulphur and phosphorus was unfortunately lost.

This number, reckoned to 100 parts, gives :

Chlorine = 65.35 per cent ;

a result sufficient to prove the identity of this liquid with the previously-described sulpho-perchloride of phosphorus.

Through the kindness of Messrs. Watts and Russell, I am enabled to add a determination of the specific gravity of the vapour of sulpho-perchloride of phosphorus. The details of the experiment are as follows :

Weight of globe filled with air, at temp. $14.5^{\circ}$ C. ( $58.1^{\circ}$ F.) ; bar. press. 29.64 inches.	} 944.10 grs.
Weight of globe filled with vapour, at temp. $203^{\circ}$ C. ( $397.4^{\circ}$ F.) ; bar. press. 29.87 inches.	} 951.60 grs.
Capacity of globe . . . . .	29.15 cub. in.
Volume of residual air, at temp. $13^{\circ}$ C. ( $55.4^{\circ}$ F.) ; bar. press. 29.77 inches.	} 9.82 cub. in.

The specific gravity of the vapour, calculated from these numbers is 5.5. Now, if we suppose 6 volumes of the vapour of pentachloride of phosphorus to unite with 4 volumes of sulphur vapour without condensation, we obtain the theoretical density 5.552. This would, therefore, appear to be the specific gravity of the vapour in question.

#### CRYSTALLINE COMPOUND.

It has already been observed, that the first distillates in the preparation of sulpho-perchloride of phosphorus deposit crystals on cooling. These will often not appear till after the lapse of several hours, or even days. In such a case, they are usually perfectly transparent and well defined, having the form of two octagonal pyramids, placed base to base, and the projecting angle at the point of juncture truncated, so as to form hexagons. The crystals thus obtained, unquestionably

## 12 ACTION OF SULPHUR UPON THE PENTACHLORIDE OF PHOSPHORUS.

sometimes contain pentachloride of phosphorus; but they comport themselves in contact with water, in a manner similar to the liquid compound just described.

I. 0.2945 grm. of well-defined crystals, drained, and exposed for awhile to a current of dry air, having been analyzed according to the process formerly described, yielded 0.964 grm. of chloride of silver, and 0.110 grm. of sulphate of baryta.

II. 0.1945 grm. of a separate crystallization, also well-defined and uniform, which was drained, and dried by means of asbestos, yielded 0.6415 grm. of chloride of silver, and 0.058 grm. of sulphate of baryta.

These numbers, reckoned to 100 parts, are :

	I.	II.
Phosphorus (by difference)	14.1	14.6
Chlorine . . .	80.7	81.3
Sulphur . . .	5.2	4.1

The proportion between the phosphorus and chlorine is evidently as 1 : 5, which would require :

	I.	II.
Phosphorus . . .	14.6	14.7
Chlorine . . .	80.7	81.3

We can scarcely suppose these crystals to be anything else than pentachloride of phosphorus, contaminated with a small quantity of the sulpho-perchloride ( $\text{PCl}_5\text{S}_4$ ), which could not be easily removed. Yet, in other analyses, where the crystals were so well defined, I have found a larger amount of sulphur; in one instance as much as 16.6 per cent. This leads me to believe either that a crystalline compound of sulphur with the pentachloride of phosphorus does exist, or that the sulpho-perchloride has itself a great tendency to cohere to the pentachloride of phosphorus. It is on this account alone, that I have specially described the crystalline body.

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*Remarks on the use of the Alkaline Carbonates, for the prevention of Incrustation in Steam Boilers.**By MR. ALFRED ANDERSON.*

The Author gave the results of his experience, that the addition of carbonates of soda and potash prevent incrustations in boilers, as Kuhlmann and others had previously observed. He states that the addition of organic matters, such as rice-meal, was also found advantageous.

*Detail of some Experiments on the Gases generated in a Sewer.**By MESSRS. MAURICE SCANLAN AND ALFRED ANDERSON.*

The experiments by the authors were made upon the sewer in Friar Street, Southwark.

The sewer was in a very foul state, being 5 feet from the floor to the roof, and containing between 3 and 4 feet of deposit, which evolved a gas of a most powerful and filthy odour. To collect it, the authors used a circular funnel of tin-plate, which was inverted in the sewage matter of the sewer, and there kept floating at the surface by a board; to the top of this funnel was connected a gutta-percha delivering tube, from which the gas was obtained. The pressure of the gas was capable of overcoming that of 4 inches of water. The greatest amount collected in 24 hours amounted to 34 cubic inches, from an area of one square foot.

The chief circumstance of chemical interest connected with this subject, upon which very little has as yet been done, is the probable existence of the bisulphide of carbon in this sewer at the time of the experiments. Being, however, a very difficult substance to detect at any time, and more particularly when mixed with so many other compounds, the observations as to its positive existence are not to be considered as conclusive. At times its peculiar odour was strongly developed. Alcohol, through which the gas had passed, acquired a peculiar odour, resembling that of onions. In distilling this solution, results were obtained, confirming, to a certain extent, the existence of sulphide of carbon.

The mixture of gas was found to consist of sulphuretted hydrogen, carburetted hydrogen, carbonic acid and phosphuretted hydrogen; of the two latter a considerable proportion. A few minutes' exposure to the gas was sufficient to produce headache and nausea. The quantitative examination of the gases was not made.

Jan. 14, 1850.

The PRESIDENT in the Chair.

The following presents were announced :

"Ofversigt af Kongl. Vetenskaps-Academiens." Förhandlingar, 1848.

"An Introductory Lecture on the importance of the study of Chemistry," and the "Arsberättelse om framstegen i Kemi," under år 1847, af L. F. Svanberg.

The January number of the "Pharmaceutical Journal," presented by the Editor.

"On the Nitro-prussides, by Lyon Playfair, Ph.D." (Phil. Trans. 1849, p. 477), from the Author.

The November number of the "Journal of the Franklin Institute," from the Institute.

The following papers were read :

### III.—*On the action of Arsenious Acid upon Albumen.*

By JOHN B. EDWARDS, F.C.S.

The attention of the Liverpool Chemists' Association has been recently directed to the above subject by Dr. Brett, in two Lectures upon Arsenic; and feeling interested in it, I have since made several experiments with a view of determining whether arsenious acid combines with albumen in atomic proportion, as believed by Professor Liebig,\* or whether such a compound is not a mere mechanical mixture of the two substances.

Liebig states, that 100 grs. of albumen combines with  $1\frac{1}{2}$  grs. of arsenious acid, and that it is in virtue of the powerful affinity existing between these bodies, that life is destroyed when they are brought together in the living organism.

I shall not notice, on this occasion, the physiological and pathological objections to this view, which were ably urged by Dr. Brett on the occasions referred to, but proceed to detail my experiments, and notice the objections arising therefrom to the "Chemical Theory."

\* Animal Chemistry, p. 361.



I took 1 gr. of opaque arsenious acid, in perfect solution in water, and 100 grs. of the glairy albumen of eggs, thoroughly mixed them by trituration, and coagulated by heat; the filtrate contained a considerable quantity of arsenious acid. The coagulate was well washed with distilled water, and the washing gave a deposit of arsenic on copper, by Reinsch's test;  $\frac{1}{2}$  oz. of the same gave, by Marsh's apparatus, a number of large stains on porcelain, which gave evidence of being arsenic, by the silver, copper, and sulphide of hydrogen tests. The coagulate was well washed, and *bruised in a mortar*, till the filtered liquid gave no indications of arsenic by Reinsch's test; the coagulate was then destroyed by sulphuric acid, neutralized, and tested by the same method; not the slightest deposit could be obtained, though boiled for half an hour, but on the addition of a solution containing  $\frac{1}{10000}$ th part of a grain of arsenious acid, the copper was immediately stained. No combination, therefore, could have taken place, for the whole of the acid was removed by patient trituration with hot water. This leads me to think that other experimenters, who have not detected arsenic in their washings, have neglected *thoroughly to break up the mechanical net-work of the coagulate*. I repeated this experiment six times, varying the proportions and the circumstances; but in each case my result was the same.

In one experiment, in which I used 100 grs. of albumen, and  $\frac{1}{4}$  gr. only of arsenious acid, I detected arsenic in five or six washings, and afterwards failed to detect it in the coagulate when decomposed. In another case, I whisked the albumen with water for some minutes, in order to destroy the organic structure, and then digested for two hours at  $98^{\circ}$  F., before coagulating; boiling water soon dissolved the whole of the arsenious acid, and none could be detected in the washed coagulate.

I then took warm sheep's blood, before congelation, 960 grs.; arsenious acid, in solution, 2 grs.; digested at  $98^{\circ}$  for three hours, and then coagulated. In this case, also, the whole of the acid was removed by boiling water. I next took 1000 grs. blood and 5 grs. arsenious acid; digested at  $98^{\circ}$ , as before, for two hours, then coagulated; by repeated boiling, I extracted the whole of the acid, the residue giving no trace by Reinsch's test; I then evaporated the washings to dryness at a low temperature, redissolved in hot water, and through the filtered solution passed a current of hydrosulphuric acid gas. I collected the tersulphide of arsenic thus formed, washed, and dried by a water-bath; the precipitate weighed 5.8 grs.

According to theory, 5 grs. of arsenious acid would be equivalent to 6.22 of the tersulphide. The correspondence of the above result proves that the whole of the acid was removed by boiling water.

I took the coagulate obtained from 2 grs. acid, and 200 grs. albumen, washed it with cold water, and gave it to a healthy young rabbit; it was violently purged, and died in about ten hours. Upon examination, the stomach was found inflamed, with extravasation of blood in patches, amounting in one or two spots to positive ulceration,—also considerable vascularity of the trachea, bronchial tubes, and intestines. The coagulate was found in the stomach *undigested*, the rabbit being a herbivorous animal; the acid had been simply dissolved by the juices of the stomach, without decomposition of the albumen.

I then offered the same quantity to a remarkably fine healthy guinea-pig; it refused to take the whole, and I suppose about  $1\frac{3}{4}$  grs. of arsenious acid was actually taken. It was purged, frothed at the mouth, and died in about sixteen hours. The stomach and other organs were found much more violently inflamed than those of the rabbit, probably on account of its living longer. *No coagulate was found in the stomach*; it was therefore digested, this being an *omnivorous* animal.

The soft organs of the rabbit were examined by Dr. Brett. He found arsenic in each. After finding a large quantity in the mucous coat of the stomach, he submitted that organ to a continuous stream of water for some time; when he could no longer detect arsenic in the washings, he decomposed the tissue with nitric acid, neutralized, and boiled for a considerable time with Reinsch's test, but was unable to detect arsenic.

I examined several organs and muscles of the guinea-pig, and found arsenic in each. I also treated the stomach of this animal in the same manner, and removed the whole of the arsenic by hot water.

Whatever objections may be raised to the first experiments with albumen, I think the facts proved by the latter are weighty arguments against Liebig's views. If water so readily extracts arsenious acid, both from the compounds formed in the laboratory, and from those which nature has prepared, surely we may conclude that its retention is simply mechanical, and affords no ground for the theory which that eminent chemist has raised upon it.

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## IV.—On the Composition of Mesitilole.

(Letter of M. A. CAHOURS to DR. A. W. HOFMANN).

In the July number of "The Quarterly Journal of the Chemical Society of London,"\* you have communicated the results of some researches on mesitilole, which have induced you to assume the expression :



for this compound, whose composition Kane had originally represented by the formula :



which subsequently had been changed into



in consequence of my determination of the vapour-density of the body in question.

In concluding your memoir, you remark that all the facts hitherto observed with regard to mesitilole are in perfect accordance with the new formula, the only exception being my determination of its vapour-density; and you leave it undecided whether the specific gravity of the mesitilole vapour, is subject to variations similar to those which have been observed with acetic, butyric, and valerianic acid, or whether the molecule of mesitilole is actually represented by 6 volumes of vapour,—an unusual mode of condensation, which would explain the difference exhibited by the properties of this body and those of cumole, which, like the other hydrocarbons, contains 4 volumes of vapour.

In preparing the mesitilole for the determination of its vapour-density, made at a comparatively early period, I had followed as accurately as possible, the directions of Kane, who states that this body boils at  $135^{\circ} \text{C}$ . I have since found, as you have yourself observed, that the boiling point of mesitilole is much higher; and I have therefore repeated the determinations with a product, carefully purified by several rectifications and a final distillation from anhydrous phosphoric acid. It boiled regularly between  $162^{\circ}$  and  $164^{\circ}$ , and exhibited exactly the composition of mesitilole.

In two determinations, made respectively at  $74^{\circ}$  and  $88^{\circ}$  higher

\* Vol. II. p. 104.

than the boiling point of the hydrocarbon, the following numbers were obtained :

	I.	II.
Temperature of the air . . . .	17°	20°
"    "    vapour. . . .	236°	250°
Excess of weight of balloon. . .	0.396 grm.	0.478 grm.
Capacity of balloon . . . . .	216 c.c.	275 c.c.
Barometer . . . . .	0 <sup>m</sup> .760	0 <sup>m</sup> .763
Residual air . . . . .	0	1
	D = 4.345	D = 4.282

The theoretical vapour-density of mesitolole, assuming this body to contain 4 volumes of vapour, is 4.146.

Thus the formula :

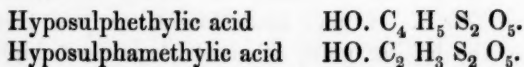


resulting from your researches on mesitolole, and confirmed by Mr. Maule's analysis of nitromesidine,\* is in perfect accordance with the specific gravity of the vapour of this compound, which ceases, moreover, to form an exception to the mode of condensation as yet generally observed with carbohydrides.

I beg you to communicate these results to the Chemical Society of London.

V.—*On the identity of Bisulphethylic with Hyposulphethylic Acids, and of Bisulphimethylic with Hyposulphamethylic acids.*  
By SHERIDAN MUSPRATT Ph. D., F.C.S.

In my paper on the "Action of Nitric Acid upon the Sulphocyanides of Ethyl and Methyl," I described acids containing *no nitrogen*, which is interesting, as they are produced by the action of *one nitrogeneous body upon another*. The following were the formulæ given for the two acids.†

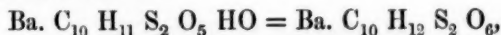


Since my results were published, others have entered upon a similar field of research, among whom I may mention Mr. Medlock, who was induced to undertake the preparation of acids in the amyl series. By the action of nitric acid upon the sulphocyanide of amyl,

\* Chem. Soc. Qu. Journ. II, 116.

† Chem. Soc. Qu. Journ. I, 45.

he procured a compound analogous in every respect to those above-mentioned. Appended to his paper, is a note by Dr. Hofmann, stating that the acid prepared by Mr. Medlock is evidently identical with the compound which MM. Gerathewohl and Erdmann obtained as a product of the decomposition of the bisulphide of amyl by means of nitric acid, although these chemists adopt a different formula for that compound. The formula which they give for the baryta-salt of their acid is :



differing from Mr. Medlock's formula,  $\text{Ba, C}_{10} \text{H}_{11} \text{S}_2 \text{O}_6$ , by one equivalent of hydrogen. In four hydrogen determinations, however, a deficiency was found, oscillating between 0.2 and 0.4 per cent, while Medlock's analysis generally gave a slight excess. A similar objection may be made to the analysis of several salts of the acid, obtained by the action of nitric acid on the bisulphide of ethyl. It would be interesting to repeat the analysis of the baryta-salt, on which the formula  $\text{H. C}_4 \text{H}_5 \text{S}_2 \text{O}_5$ , assigned to this acid is principally founded.

I have intended, for some time, to recur to the bisulphethylic acid, considering that its description and properties correspond very closely with those of my acid ; yet I have not, until now, had an opportunity to decide the question as to their identity : moreover, the repulsive qualities of bisulphide of ethyl are almost a sufficient reason to debar any one from preparing the compound. It is extremely difficult, with acids containing a small per centage of hydrogen, to arrive at its exact amount, even when the greatest accuracy is exercised ; consequently I was determined to prepare the baryta-salt of Löwig's acid, and to ascertain the exact amount of baryta ; and if that amount corresponded with the quantity of baryta in the salt, obtained by the action of nitric acid upon the sulphocyanide of ethyl, the identity of the two would be proved, and the correctness of my formula established.

#### PREPARATION OF BISULPHIDE OF ETHYL.

It is extremely difficult to obtain this body in large quantities, and, unless the materials employed are well prepared, the stench is insufferable : my clothes have retained it for weeks.

The best mode of procedure appears to be, to distil equal portions of concentrated solutions of sulphovinate of lime and tersulphide of potassium in a retort, having a capacity ten times the volume of the mixture, to prevent any of the solution passing over into the receiver, which it is apt to do, owing to violent intumescence that occurs. As

the mass becomes viscid, the oil that drops over must be repeatedly washed with distilled water, and then rectified several times over chloride of calcium. It has a most disgusting smell when crude, but after rectification the smell is only slightly alliaceous. It is sparingly soluble in water, but is copiously dissolved by alcohol and ether: it burns with a blue flame, giving sulphurous acid. In the air it is unchanged, but potash slowly decomposes it.

#### PREPARATION OF THE ACID.

Equal parts of bisulphide of ethyl and tolerably strong nitric acid were introduced into a retort adapted to a Liebig's condenser. A gentle heat was applied during the process. The action was most violent, nitrogen, carbonic acid, and nitrous acid passing off: sulphuric acid was also produced during the operation, but I found the quantity depended upon the strength of the acid employed. The distillate was repeatedly returned to the retort to decompose all the oil. When the elimination of gas had ceased, the liquid was evaporated over a water bath, to expel the least trace of nitric acid. A fluid like oil of vitriol remained, possessing a slight alliaceous odour. This was dissolved in water, saturated with pure carbonate of baryta, and filtered to remove the excess of carbonate and any sulphate of baryta. The filtrate, on slow evaporation, afforded large rhombohedral crystals of hyposulphethyrate of baryta. These crystals were dissolved in water, and precipitated by an excess of absolute alcohol and recrystallized.

The following is an analysis of the salt dried at 100° C.

0.1212 grms. of substance gave 0.0797 grms. of sulphate of baryta  
= 0.0524 grms. of baryta = 43.23 per cent.

From a pretty considerable quantity of the salt I precipitated the baryta by sulphuric acid, and filtered. I digested the filtrate with carefully prepared carbonate of lead, refiltered and decomposed the lead solution by sulphide of hydrogen, separated the sulphide of lead, and evaporated the filtrate on a water bath.

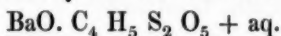
A portion of it left in a cold place over sulphuric acid *in vacuo*, afforded colourless needles, extremely deliquescent, and having a feeble odour of garlic. The deliquescent mass was mixed with water and carbonate of baryta, filtered, and the filtrate evaporated. Very fine crystals of the rhombohedral system settled down, which were dried over sulphuric acid.



## ANALYSIS OF THESE CRYSTALS.

0·801 grms. of the crystals dried at 100° C. gave 0·0386 grms. of water.

These results agree exactly with the annexed formula :



Centesimally represented :

		Theory.	Found.
Hyposulphethylate of baryta . . .	178	95·19	„
Water . . . . .	9	4·81	4·81
		<hr/>	
		100·00	

This salt, when dried at 100° C. yielded the following numbers :

0·410 grms. of salt burnt with chromate of lead gave 0·204 grms. of carbonic acid and 0·111 grms. of water.

0·1701 grms. of salt, treated with potash and nitrate of potash gave 0·2210 grms. of sulphate of baryta = 0·0302 grms. of sulphur.

0·2399 salt, dried at 100° C. gave 0·1580 grms. of sulphate of baryta = 0·1039 grms. of baryta.

Centesimally represented :

			Theory.	Found.	
				Analysis of the Baryta-salt of the acid produced by the action of nitric acid on the Bisulphide of Ethyl.	Analysis of the Baryta-salt of the acid produced by the action of nitric acid on the Sulphocyanide of Ethyl.
4 eq. Carbon . . .	24	13·49	13·53	13·16	
5 „ Hydrogen . . .	5	2·82	3·00	3·05	
2 „ Sulphur . . .	32	17·97	17·75	17·56	
5 „ Oxygen . . .	40	22·47	22·42	22·97	
1 „ Baryta . . .	77	43·25	43·30	43·26	
		<hr/>	<hr/>	<hr/>	<hr/>
		178	100·00	100·00	100·00

On referring to the preceding analysis, there is every ground for asserting, that the baryta-salt of the acid produced by the action of nitric acid on the bisulphide of ethyl, is identical with the baryta-salt of the acid produced by the action of nitric acid on the sulphocyanide of ethyl. Löwig's baryta-salt yields, theoretically, 3·35 per cent of hydrogen; mine gives 2·82 per cent. Analysis gives me 3·00 and 3·05 per cent. Kopp found in the baryta-salt of the acid produced by

the action of nitric acid upon the bisulphide of ethyl, 43·66 per cent of baryta, while Löwig gives 44·83 per cent of baryta *in the same salt*, a difference sufficiently accounting for the formula which the latter assumed.

Appended are the four determinations that have been made :

Baryta in the acid from the bisulphide of ethyl . . . . .	43·66 per cent—Kopp*.
Baryta in the acid from the same source . . . . .	43·23 „ „ —Muspratt.
Second determination . . . . .	43·30 „ „ —Ditto.
Baryta in the acid produced from the sulphocyanide of ethyl by the action of nitric acid. . . . .	43·26 „ „ —Muspratt.

#### PREPARATION OF THE ACID FROM BISULPHIDE OF METHYL.

The bisulphide of methyl was treated similarly to the ethyl compound. I remarked, on evaporating the decomposed bisulphide on the water bath, that a most stifling vapour passed off, which excited a flow of tears. This, however, was not the case when the purified bisulphide of methyl was employed.

#### PREPARATION OF THE BARYTA-SALT.

The acid was mixed with an excess of carbonate of baryta, filtered, and the filtrate precipitated by absolute alcohol. Very fine splendid needles were deposited, which, when dried at 100° C., gave the annexed quantities of baryta :

First determination ; 0·2140 grms. of salt gave 0·1520 grms. of sulphate of baryta, equivalent to 0·1000 grms. of baryta = 46·72 per cent.

Second determination ; 0·2310 grms of salt gave 0·1650 grms. of sulphate of baryta, equivalent 0·1085 grms. of baryta = 46·97 per cent.

I shall append the above two determinations, collaterally with the one I previously made with the baryta-salt obtained from the acid produced by the action of nitric acid on the sulphocyanide of methyl.

Baryta-salt of the acid obtained by the action of nitric acid on the bisulphide of methyl.

\* Löwig's *Chemie der organischen Verbindungen*. II. Band, S. 427.



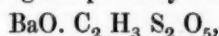
Centesimally represented :

I . . . . .	46.72 baryta.
II . . . . .	46.97 „

Baryta-salt of the acid obtained by the action of nitric acid on the sulphocyanide of methyl :

I . . . . .	46.74 per cent of baryta.
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The following formula agrees perfectly with the above :



and yields 46.95 per cent baryta by theory ; a sufficient proof of the identity of the two methyl-acids.

Having obtained such satisfactory results with regard to the identity of the two ethyl acids with each other, and of the two methyl acids with each other, I did not think it necessary to prepare the bisulphide of amyl, so as to ascertain whether the acids of Erdmann and Medlock were identical. When identity is proved in the ethyl series, with regard to two acids, we may, with a degree of certainty, assume identity in corresponding series, such as those of methyl and amyl ; and, although the latter series are not so extended as the former, still the analogues of all the sulphur and oxygen compounds of the ethyl combinations will, I am convinced, be discovered long before. When this is the case, more decided conclusions may be drawn with regard to the basyles and salt radicals, upon which the whole fabric of chemical theory is at present based.

Although the number of compounds in Organic Chemistry is very great, yet I feel convinced that a repetition of old investigations, by skilful hands, will tend to reduce their number ; for, with regard to the accurate determination of a formula, very much depends upon the perfection of the apparatus employed and the accuracy of the manipulator.

I shall, in conclusion, give the formulæ for the two acids which have been discussed :

Hyposulphethylic acid	H. C <sub>4</sub> H <sub>5</sub> S <sub>2</sub> O <sub>6</sub> , or HO. C <sub>4</sub> H <sub>5</sub> S <sub>2</sub> O <sub>5</sub> ,
Hyposulphamethylic acid	H. C <sub>2</sub> H <sub>3</sub> S <sub>2</sub> O <sub>6</sub> , or HO. C <sub>2</sub> H <sub>3</sub> S <sub>2</sub> O <sub>5</sub> .

Feb. 4, 1850.

WILLIAM ALLEN MILLER, M.D., V.P., in the Chair.

Mr. George Maule was elected a Fellow of the Society.

The following Presents were announced :

"The Pharmaceutical Journal," for February, from the Editor.

"Proceedings of the Philosophical Society of Glasgow," Vol. III, No. 1.

"Experimental Investigation into the amount of water given off by Plants during their growth," and "On Agricultural Chemistry," by J. B. Lawes, presented by J. H. Gilbert, Ph. D.

"Address delivered at the Anniversary Meeting of the Geological Society of London, on the 16th of February, 1849, by Sir Henry T. De la Beche, C.B., F.R.S.," presented by the Author.

"On Benzole," by C. B. Mansfield, from the Author.

The following Papers were read :

"On some of the Salts of Carbonic Acid," by Mr. N. Samuelson.

#### VI.—*Observations on Etherification.*

By THOMAS GRAHAM, F.R.S., F.C.S., &c.

In the ordinary process of etherizing alcohol by distilling that liquid with sulphuric acid, two distinct chemical changes are usually recognized ; namely, first, the formation of sulphovinic acid, the double sulphate of ether and water ; and secondly, the decomposition of the compound named, and liberation of ether. The last step, or actual separation of the ether, is referred to its evaporation, in the circumstances of the experiment, into an atmosphere of steam and alcohol vapour, assisted by the substitution of water as a base to the sulphuric acid, in the place of ether. The observation, however, of M. Liebig, that ether is not brought off by a current of air passing through the heated mixture of sulphuric acid and alcohol, is subversive of the last explanation, as it demonstrates that the physical agency of evaporation is insufficient to separate ether. Induced to try whether ether could not be formed without distillation, I obtained results which appear to modify considerably the views which can be taken of the nature of the etherizing process.

The spirits of wine or alcohol always employed in the following experiments, was of density 0.841, or contained 83 per cent of absolute alcohol.

*Expt. 1.* One volume of oil of vitriol was added to four volumes of alcohol, in a gradual manner, so as to prevent any considerable rise

of temperature. The mixture was sealed up in a glass tube, 1 inch in diameter and 6.6 inches in length, of which the liquid occupied 5.2 inches, a space of 1.4 inch being left vacant, to provide for expansion of the liquid by heat. The tube was placed in a stout digester containing water, and safely exposed to a temperature ranging from  $284^{\circ}$  to  $352^{\circ}$  ( $140^{\circ}$  to  $178^{\circ}$  C.) for one hour.

No charring occurred, but the liquid measured on cooling, 5.25 inches in the tube, and divided into two columns, the upper occupying 1.75 inches, and the lower 3.5 inches of the tube. The former was perfectly transparent and colourless, and on opening the tube, was found to be ether, so entirely free from sulphurous acid, that it did not affect the yellow colour of a drop of the solution of bichromate of potash. The lower fluid had a slight yellow tint, but was transparent. It contained some ether, but was principally a mixture of alcohol, water and sulphuric acid. The salt formed by neutralizing this acid fluid with carbonate of soda, did not blacken when heated, from which we may infer that little or no sulphovinic acid was present.

The principal points to be observed in this experiment, are its entire success as an etherizing process, without distillation, without sensible formation of sulphovinic acid, and with a large proportion of alcohol in contact with the acid, namely, two equivalents of the former nearly, to one of the latter. When the proportion of the alcohol was diminished, the results were not so favourable.

*Expt. 2.* A mixture of one volume of oil of vitriol and two volumes of alcohol, sealed up in a glass tube, was heated in the same manner as the last. The liquid afterwards appeared of an earthy-brown colour by reflected light, and was transparent and red by transmitted light. Only a film of ether was sensible after twenty-four hours, floating upon the surface of the dark fluid.

*Expt. 3.* With a still smaller proportion of alcohol, namely one volume of oil of vitriol with one volume of alcohol, which approaches the proportions of the ordinary etherizing process, a black, opaque liquid was formed at the high temperature, thick and gummy, without a perceptible stratum of ether, after standing in a cool state.

Crystals of bisulphate of soda, containing a slight excess of acid, were found to etherize about twice their volume of alcohol, in a sealed tube, quite as effectually as the first proportion of oil of vitriol, when heated to the same temperature. The two liquids found in the tube were colourless, no sulphurous acid appeared, and only a minute quantity of sulphovinic acid. Crystals of bisulphate of soda, which were formed in an aqueous solution and without an

excess of acid, had still a sensible but much inferior etherizing power.

*Expt. 4.* A mixture was made of oil of vitriol with a still larger proportion of alcohol, namely, 1 volume of the former and 8 of the latter, or nearly 1 equivalent of acid to 4 equivalents of alcohol. This mixture was sealed up in a tube and heated for an hour between  $284^{\circ}$  and  $317^{\circ}$  ( $140^{\circ}$  and  $158^{\circ}$  C.), which appeared sufficient for etherizing it. A second exposure for another hour to the same temperature did not sensibly increase the ether product. The column of ether measured 1.25 in the tube, and the acid fluid below 2.5 inches. Both fluids were perfectly colourless.

It thus appears to be unnecessary to exceed the temperature of  $317^{\circ}$  ( $158^{\circ}$  C.) in this mode of etherizing, and that the proportion of alcohol may be increased to eight times the volume of the oil of vitriol without disadvantage.

*Expt. 5.* The proportions of the first experiment were again used, namely, 1 volume of oil of vitriol with 4 volumes of alcohol, and the mixture heated as in the last experiment to  $317^{\circ}$  ( $158^{\circ}$  C.). The upper fluid, or ether, measured 1.1 inch in the tube, the lower fluid 2.65 inches. The latter had a slight yellow tint, like nitrous ether, but only just perceptible. It gave, when neutralized by chalk:

Sulphate of lime	. . .	83.11 grains.
Sulphovinate of lime	. . .	4.91 „

The last salt was soluble in alcohol, and crystallized in thin plates.

Here again the formation of sulphovinic acid in a successful etherizing process is quite insignificant.

New results at  $317^{\circ}$ , from the other proportions of 1 volume of oil of vitriol with 1 and 2 volumes of alcohol, were quite similar to those obtained in experiments 2 and 3, at the higher temperature of  $352^{\circ}$ . In none of these experiments, did there appear to be any formation of olefiant gas, and the tubes could always be opened, when cool, without danger.

Neither glacial phosphoric acid nor crystallized biphosphate of soda etherized alcohol to the slightest degree, when heated with that substance in a sealed tube, to  $360^{\circ}$  ( $182^{\circ}$  C.). Even chloride of zinc produced no more, at the same temperature, than a trace of ether, perceptible to the sense of smell.

*Expt. 6.* To illustrate the ordinary process of ether-making, a mixture was prepared, as usually directed, of:

100 parts of oil of vitriol,
48 „ of alcohol (0.841),
18.5 „ of water.

This liquid was sealed up in a glass tube, and heated to  $290^{\circ}$  ( $143^{\circ}$  C.) for one hour. It became of a dark greenish-brown colour, and opalescent, with a gummy looking matter in small quantity. No stratum of ether formed upon the surface of the fluid.

The tube was opened and the fluid divided into two equal portions. One of the portions was mixed with half its volume of water, and the other with half its volume of alcohol, and both sealed up in glass tubes and exposed again to  $290^{\circ}$  for one hour.

It would be expected, on the ordinary view of water setting free ether from sulphovinic acid, that much ether would be liberated in the mixture above, to which water was added. The ether which separated, however, amounted only to a thin film, after the liquid had stood for several days. In the other liquid, on the contrary, to which alcohol was added, the formation of ether was considerable, a column of that liquid appearing, which somewhat exceeded half the original volume of the alcohol added. In fact, the sulphovinic acid was nearly incapable of itself of yielding ether, even when treated with water. But it was capable of etherizing alcohol added to it, in the second mixture, like bisulphate of soda or any other acid salt of sulphuric acid.

The conclusions which I would venture to draw from these experiments are the following.

The most direct and normal process for preparing ether, appears to be, to expose a mixture of oil of vitriol with from four to eight times its volume of alcohol of 83 per cent, to a temperature of  $320^{\circ}$  ( $160^{\circ}$  C.), for a short time. Owing to the volatility of the alcohol, this must be done under pressure, as in the sealed glass tube. The sulphuric acid then appears to exert an action upon the alcohol, to be compared with that which the same acid exhibits when mixed in a small proportion with the essential oils. Oil of turpentine, mixed with one-twentieth of its volume of sulphuric acid, undergoes an entire change, being chiefly converted into a mixture of two other hydrocarbons, terebene and colophene, one of which has a much higher boiling point and greater vapour-density than the oils of turpentine. This hydrocarbon does not combine with the acid, but is merely increased in atomic weight and gaseous density without any further derangement of composition, by a remarkable polymerizing action (as it may be termed) of the sulphuric acid. So of the hydrocarbon of alcohol; its density is doubled in ether, by the same polymerizing action. Chloride of zinc effects, with alcohol, at an elevated temperature, a polymeric catalysis of the latter, of the same

character, but in which hydrocarbons are formed, of even greater density and free from oxygen.

This view of etherification is only to be considered as an expression of the contact-theory of that process which has long been so ably advocated by M. Mitscherlich.

The formation of sulphovinic acid appears not to be a necessary step in the production of ether; for we have found that the etherizing proceeded most advantageously with bisulphate of soda, or with sulphuric acid mixed with a large proportion of alcohol and water, which would greatly impede the production of sulphovinic acid. It appears, indeed, that the combination of alcohol with sulphuric acid, in the form of sulphovinic acid, greatly diminishes the chance of the former being afterwards etherized; for, when the proportion of oil of vitriol was increased in the preceding experiments, which would give much sulphovinic acid, the formation of ether rapidly diminished. The previous conversion of alcohol into sulphovinic acid, appears, therefore, to be actually prejudicial, and to stand in the way of its subsequent transformation into ether.

The operation of etherizing has attained a kind of technical perfection in the beautiful contiguous process now followed. The first mixture of alcohol and sulphuric acid is converted into sulphovinic acid, the sulphate of ether and water, which acid salt appears to be the agent which polymerizes all the alcohol afterwards introduced into fluid. Bisulphate of soda, with a slight excess of acid, acts upon alcohol in the same manner, and its substitution for the acid sulphate of ether would have a certain interest, in a theoretical point of view, although a change of no practical importance in the preparation of ether.

Sulphuric acid does not appear to be adapted for the etherizing of amylic alcohol. M. Balard, by distilling these substances together, obtained a variety of hydrocarbons, some of them of great density, but no ether. The polymerizing action of the sulphuric acid appears to advance beyond the ether stage. I have varied the experiment by heating amylic alcohol, in a close tube, to  $350^{\circ}$  ( $176^{\circ}$  C.) with oil of vitriol, to which 1, 2, 3, 4, and even 6 equivalents of water had been added, without obtaining anything but the hydrocarbons of Balard. The formation of these was abundant, even with the most highly hydrated acid, and with a very moderate colouration of the fluid.

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VII.—*On a Natural Alloy of Silver and Copper from Chile.**By MR. FREDERICK FIELD.*

The alloy was taken from a mine about twenty leagues east of Coquimbo, and six from the Cordillera of the Andes.

It was perfectly free from oxygen, sulphur, &c., and other substances usually found combined with metals in nature, having exactly the appearance of an artificially smelted product from a copper furnace. 100 grs. taken from the centre of a large mass, was found to contain, on analysis :

Copper	.	.	.	.	.	.	98.91
Silver	.	.	.	.	.	.	1.09
							<hr/>
							100.00

The quantity of silver, however, was very variable. One portion of the alloy had almost a whitish appearance, and, on being separated by the chisel and analysed, gave :

Copper	.	.	.	.	.	.	92.40
Silver	.	.	.	.	.	.	7.60
							<hr/>
							100.00

I have a large specimen, weighing more than a pound, which I hope to have the pleasure of sending to the Society's Museum by the first opportunity.

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Feb. 18, 1850.

The PRESIDENT in the Chair.

The Rev. Bath Power and H. Yates Finch, Esq., were elected Fellows of the Society.

The following Papers were read :

“ On some Salts of Chromic Acid,” by Mr. J. Danson.

VIII.—*Researches on the Organic Radicals ; Part II, AMYL.*

By E. FRANKLAND, PH. D., F.C.S., PROFESSOR OF METALLURGY  
IN THE COLLEGE FOR CIVIL ENGINEERS, PUTNEY.

In studying the decomposition of iodide of ethyl by zinc,\* I obtained, in addition to ethyl and zinc-ethyl, two bodies as secondary products, having the empirical formulæ,  $C_2H_2$  and  $C_2H_3$ ; the former agreeing exactly, so far as its reactions were followed out, with olefiant gas, and the latter having the same composition and specific gravity as methyl; but, as both these bodies are permanent gases, it was difficult to prove their complete identity with olefiant gas, and with the methyl procured in the decomposition of cyanide of ethyl by potassium,† and by the electrolysis of acetic acid;‡ owing, however, to the much higher atomic weight and vapour-density of the amyl compounds, it appeared highly probable that, if the iodide of this radical be similarly decomposed by zinc, the secondary products of decomposition corresponding to the two bodies above-named, will exist at ordinary temperatures as liquids, the re-actions and physical character of which, would lead to the discovery of their rational constitution, as well as that of the two gaseous bodies before alluded to. These considerations induced me to attempt next the isolation of the hitherto hypothetical radical amyl, in preference to any of the other members of the same series.

For the preparation of the iodide of amyl, which served for the experiments detailed in the following pages, a modification of the process described by Cahours§ was employed. Four parts of iodine were dissolved at intervals in seven parts of pure fusel-oil, and between each addition of iodine a stick of phosphorus was suspended in the liquid until the latter became nearly colourless. The fluid thus obtained had an oily consistence, and emitted copious fumes of hydriodic acid when exposed to the air; on being submitted to distillation in an oil-bath, a colourless liquid containing much free hydriodic acid and unchanged fusel-oil, passed over into the receiver, whilst a non-volatile, thick, oily fluid, insoluble in water,

\* Chem. Soc. Qu. Journ. II., 265.

† Chem. Soc. Qu. Journ. I., 60.

‡ Chem. Soc. Qu. Journ. II, 173.

§ Ann. Ch. Phys. LXX, 95.



and re-acting strongly acid remained in the retort.\* The distillate was washed with a small quantity of water to remove the hydriodic acid, and after standing twenty-four hours over chloride of calcium, was redistilled: it began to boil at  $120^{\circ}$  C. (the boiling-point of iodide of amyl as given by Cahours); but the thermometer gradually rose to  $146^{\circ}$  C., at which temperature the last  $\frac{1}{3}$  of the fluid distilled over, and was collected in a separate receiver. If the whole of the hydriodic acid had not been removed by the previous washing with water, the liquid generally became coloured violet by free iodine, during this second distillation; but the coloration was easily removed by a subsequent rectification over mercury, and the iodide was then quite pure. The first  $\frac{2}{3}$  of the distillate which pass over between  $120^{\circ}$  and  $146^{\circ}$  C. also contains much iodide of amyl, and may be advantageously employed for the preparation of a further quantity, by adding more iodine and phosphorus in the relative proportions already given.

Iodide of amyl is a colourless and transparent liquid, refracting light strongly, possessed of a weak, ethereal odour, and a sharp, biting taste: it boils at  $146^{\circ}$  C. under a pressure of  $175^{\text{mm}}$ , and not at  $120^{\circ}$  C. as stated by Cahours: its specific gravity is 1.51113 at  $11.5^{\circ}$  C.

Burnt with oxide of copper 0.3600 grm. gave 0.4003 grm. carbonic acid, and 0.1797 grm. water; numbers which give the following per centage composition:

	Calculated.	Found.
C <sub>10</sub> . . . . .	30.36	30.32
H <sub>11</sub> . . . . .	5.55	5.55
I . . . . .	64.09	—
	<hr/> 100.00	

Some preliminary experiments shewed, that iodide of amyl is acted upon by zinc with much more difficulty than the corresponding ethyl compound, which seems to be principally owing to the very sparing solubility of iodide of zinc in the surrounding liquid, and also to the comparatively low temperature at which iodide of amyl, heated alone as well as with zinc, is decomposed into free hydriodic acid and other gaseous products, which I have not as yet more closely investigated. In consequence of these difficulties, it requires a very nice management of the temperature to effect anything like a perfect

\* This fluid, which is formed in large quantity, and probably contains a compound of an acid of phosphorus with oxide of amyl, merits closer investigation.

decomposition of the iodide by zinc alone. This led me to employ an amalgam of that metal, which answered the purpose admirably; for, on being subsequently heated with the liquid iodide, the pasty metallic mass becomes perfectly fluid, and, owing to the agitation of the boiling liquid, continually presents a fresh and bright surface. This amalgam acts considerably upon the iodide at the ordinary boiling-point of the latter, but exposed to a temperature about  $10^{\circ}$  C. higher, in a sealed tube, it undergoes decomposition with tolerable rapidity, no gases are evolved, but, on distilling the resulting liquid, the variation of the boiling-point from  $30^{\circ}$  C. to  $160^{\circ}$  C. shews the liquid to be a mixture of at least two bodies.

For the purpose of submitting the iodide of amyl to the action of zinc-amalgam under pressure, I employed strong glass tubes about  $\frac{3}{4}$  inch in diameter and 14 inches long, closed at one end, and having the other drawn out to about  $\frac{3}{8}$  inch in diameter and 3 inches long. Each of these tubes was filled to the height of 1.5 in. with zinc-amalgam of a pasty consistence, above which was placed a layer of granulated zinc 2 inches deep, which afterwards gradually dissolved in the mercury, as the amalgam became diluted by the action of the liquid iodide. From  $\frac{3}{4}$  oz. to 1 oz. of the iodide of amyl being then introduced, the open end of the tube was drawn out to a fine orifice, which, after boiling the included fluid for a moment to expel the air, was hermetically sealed with a mouth-blowpipe. The tube was then immersed in an oil bath to the depth of about 3 inches, and maintained at a temperature varying from  $160^{\circ}$  to  $180^{\circ}$  C. for several hours. Subsequently, and after being allowed to cool, so much of the drawn-out extremity was broken off as admitted of the introduction of from 1 to 2 grms. of potassium, and the tube, being again hermetically closed, was subjected to the same temperature as before for about an hour. When perfectly cool, the upper part was again cut off, and a cork and bent tube adapted to the orifice. The bent tube led to a receiver which was kept cool by a freezing mixture of dilute sulphuric acid and snow; the decomposition tube was now immersed to nearly its whole length in a water-bath, the temperature of which never exceeded  $80^{\circ}$  C.; about  $\frac{3}{4}$  of the liquid contents of the tube distilled over; the receiver was then changed, and the water-bath being removed, the decomposition tube was carefully heated by means of a spirit-lamp, until the remaining fluid had come over.

As valyl, according to Kolbe,\* boils at  $108^{\circ}$  C., and the addition of the elements  $C_2 H_2$  to the same volume of vapour must necessarily cause a considerable elevation of the boiling-point, it appeared highly

\* Chem. Soc. Qu. J., II, 161.

probable that the amyl, if separated as such, would be found in the less volatile liquid, which supposition was also strengthened by the analogous decomposition of iodide of ethyl; I therefore first submitted the last-obtained product to investigation. This liquid, which was colourless and possessed of a peculiar penetrating odour, was not in the least acted upon by potassium, even at its boiling point, the fused metal remaining at the bottom of the fluid, like a globule of mercury, and presenting a surface of remarkable brilliancy. On being distilled, its boiling point rapidly rose to  $155^{\circ}$  C., and remained nearly constant at this temperature until the whole had passed over. The fluid which distilled at  $155^{\circ}$  C. was collected separately and submitted to analysis.

I. 0.1757 grm. burnt with oxide of copper\* gave 0.5426 grm. carbonic acid, and 0.2433 grm. water.

II. 0.2000 grm. gave 0.6207 grm. carbonic acid, and 0.2732 grm. water.

III. 0.1101 grm. gave 0.1523 grm. water.

These numbers agree closely with those calculated from the formula of the hitherto unisolated radical amyl:



	Calculated.		Found.			
			I.	II.	III.	MEAN.
$\text{C}_{10}$ . . . .	60	84.5	84.2	84.6		84.4
$\text{H}_{11}$ . . . .	11	15.5	15.4	15.2	15.4	15.3
	71	100.0	99.6	99.8		99.7

A determination of the specific gravity of its vapour yielded the following results confirmatory of the above formula:

Weight of liquid used . . . . .	1670 grm.
Observed vol. of vapour . . . . .	46.5 cbc.
Temperature . . . . .	$190.5^{\circ}$ C. .
Height of barometer . . . . .	738.1 <sup>mm</sup>
„ „ inner column of mercury. . . . .	10.0 <sup>mm</sup>

From which the specific gravity was calculated to be 4.8989.

Amyl is a colourless, pellucid liquid possessing a slight ethereal odour and a burning taste; exposed to a cold of  $-30^{\circ}$  C., it becomes

\* At the conclusion of each analysis, a stream of oxygen evolved from perchlorate of potash placed at the further end of the combustion tube, was led over the reduced oxide of copper, until the latter was completely reoxidized. The material used in analysis No. II, was a separate preparation.

thick and oily, but does not solidify; its specific gravity in the liquid form is 0.7704 at 11° C., that of its vapour 4.9062. According to the above determination of the specific gravity of its vapour, this radical contains 5 vols. carbon vapour and 11 vols. hydrogen condensed to 1 vol., and is thus, in this respect, perfectly analogous to methyl, ethyl, and valyl.

5 vol. carbon vapour	.	.	.	.	4.1461
11 vol. hydrogen	.	.	.	.	0.7601
<hr/>					
1 vol. amyl vapour.	.	.	.	.	4.9062
Found by experiment	.	.	.	.	4.8989

Amyl boils at 155° C. at a pressure of 728<sup>mm</sup>; it does not ignite at ordinary temperatures; but on being heated, its vapour burns with a white smoky flame. It is insoluble in water, but miscible in all proportions with alcohol and ether. It is not affected by fuming sulphuric acid, and is but very slowly oxidized by boiling fuming nitric acid, or by a mixture of nitric and sulphuric acids. During this oxidation, the liquid acquires the odour of valerianic acid.

The action of chlorine and bromine, as well as of oxidizing agents, upon amyl and the two bodies noticed below, will be described in a future communication.

It still remained to examine the very volatile liquid which had distilled over from the decomposition tube, at a temperature not exceeding 80° C. This liquid possessed a very powerful, penetrating, and rather disagreeable odour, much resembling that of the body  $C_8H_8$ , evolved during the electrolysis of valerianic acid, and a taste at first rather sweet, but afterwards nauseous and tar-like. It was so volatile, that when the thin glass vessel containing it was held in the hand, it immediately entered into ebullition.

To ascertain the relative quantities of carbon and hydrogen contained in this liquid, and thus obtain some clue to its composition, a portion of it was burnt with oxide of copper.

0.1577 grm. yielded 0.4870 grm. carbonic acid and 0.2260 grm. water, numbers which indicate the following per centage composition:

Carbon	.	.	.	.	84.2
Hydrogen	.	.	.	.	15.9
					<hr/>
					100.1

Since, in the decomposition of iodide of ethyl by zinc, a portion of the separated radical is transformed into equal volumes of  $C_2H_2$  and

$C_2H_3$ ,\* it was not improbable that a similar decomposition of amyl had here taken place, and that this volatile liquid contained the products, which would, in fact, yield an analytical result similar to the one just given. To ascertain if this were the case, I availed myself of the property which anhydrous sulphuric acid seems to possess of combining with carbo-hydrogens of the form  $C_nH_n$ , and leaving unacted upon those of the form  $C_n + H_{(n+1)}$ ; and, as the liquid was easily converted into a temporary gas, I submitted it to the following experiment, which, at the same time, gave the specific gravity of its vapour.

A small and very thin glass bulb was filled as perfectly as possible with a weighed quantity of the fluid, hermetically sealed, and then introduced into a short eudiometer filled with quicksilver, and inverted in an iron trough containing the same metal, to which heat could be conveniently applied. A long glass cylinder, open at both ends, was then lowered perpendicularly over the eudiometer, and immersed to the depth of about 2 inches in the mercury; it was then filled to such a height with water, that the enclosed eudiometer was completely beneath the surface. Heat being afterwards applied below the mercury trough, the glass bulb in the eudiometer soon burst, and the enclosed fluid became converted into vapour. When the water in the glass cylinder had boiled for some time, the volume of the vapour was accurately noted, as well as the height of the barometer and the elevation of the column of mercury in the eudiometer above that in the trough outside the glass cylinder. The water and cylinder were then removed, and the whole apparatus allowed to cool until the vapour had again assumed the liquid form: the temperature at which this took place was only a very few degrees above that of the surrounding atmosphere. A coak bullet, saturated with a solution of anhydrous sulphuric acid in Nordhausen acid was then introduced: on coming in contact with the carbo-hydrogen, a quantity of vapour, equal to about half the original volume, was rapidly formed, and maintained the gaseous condition at the temperature of the surrounding air, although it was immediately condensed by cooling the tube a few degrees,—a proof that the body not absorbed by sulphuric acid has its boiling point near to, but lower than, that absorbed by the acid. Although the action of the sulphuric acid appeared to be nearly instantaneous, yet, in order to be sure that the absorption was quite complete, the coak bullet was allowed to remain in the vapour for half-an-hour, and the temperature of the mercury was raised  $10^0$  or  $12^0$  C., before its withdrawal, in order

\* Chem. Soc. Qu. J. vol. II, p. 281.

to ensure the complete volatilization of the body left unabsorbed by the acid. On coming in contact with moist air, the bullet still fumed strongly, which was a proof that the acid had been present in excess. A ball of hydrate of potash was now introduced, and left in the vapour until every trace of sulphurous acid and vapours of sulphuric acid had been absorbed—in fact, until the moment before the volume of the remaining vapour was read off, which was effected, along with the collateral observations, after the glass cylinder and water had been replaced—and the whole heated to  $42^{\circ}\text{C}$ . A higher temperature was considered undesirable, lest the elasticity of the vapour of the sulphuric acid compound, traces of which still adhered to the sides of the eudiometer, should introduce inaccuracy into the observation. The following results were obtained :

## I.

	Absd. vol.	Temp. C.	Diff. of mer- cury level.	Barom.	Cor. vol. at $0^{\circ}\text{C}$ . and $760^{\text{mm}}$ press.
Vol. of vapour (dry)	18.7 cbc.	$100^{\circ}$	$109.2^{\text{mm}}$	$756.1^{\text{mm}}$	11.65
Vol. after action of sulph. acid (dry)	8.9 „	$42.0^{\circ}$	$142.2$ „	$752.2$ „	6.20

## II.

Weight of liquid used	.	.	.	.	0.0366 grm.
Observed vol. of vapour	.	.	.	.	18.7 cbc.
Height of barometer	.	.	.	.	$760.3^{\text{mm}}$
Difference of mercury level	.	.	.	.	$109.2$ „
Temperature	.	.	.	.	$100^{\circ}\text{C}$ .
Specific gravity of vapour	.	.	.	.	2.4179

According to experiment No. I., it follows that 11.65 vols. of the vapour contained 5.45 vol. absorbable by sulphuric acid, and 6.20 vol. unabsorbable by that acid; or 100 vols. consisted of:

Vapour absorbable by $\text{SO}_3$	.	.	.	.	46.78
Vapour unabsorbable by $\text{SO}_3$	.	.	.	.	53.22
					<hr/> 100.00

These results are exactly analogous to those yielded by the gases produced by the transformation of ethyl into equal volumes of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_3$ ,\* and indicate that a portion of the

\* Chem. Soc. Qu. J. II, 277.



amyl has been similarly transformed into equal volumes of the hitherto unknown carbo-hydrogens having the empirical formulæ :



and



The specific gravity of the vapour of a mixture containing these two bodies in the proportions indicated by experiment, No. I. would be 2.45533, as shewn by the following calculation :

$$\text{C}_5\text{H}_5 \begin{cases} 2\frac{1}{2} \text{ vols. carbon vapour} = 2.07305 \\ 5 \text{ vols. hydrogen} = 0.34550 \end{cases}$$

$$\text{Condensed to 1 vol.} = 2.41855 \times 46.78 = 113.140$$

$$\text{C}_5\text{H}_6 \begin{cases} 2\frac{1}{2} \text{ vols. carbon vapour} = 2.07305 \\ 6 \text{ vols. hydrogen} = 0.41460 \end{cases}$$

$$\text{Condensed to 1 vol.} = 2.48765 \times 53.22 = 132.393$$

$$\underline{245.533}$$

$$\underline{100}$$

$$= 2.45533$$

A number which closely corresponds with that found by direct experiment, No. II. (2.4179).

It now only remained to separate one of these compounds in a state of perfect purity, to prove the existence of both. To effect this, the mixture of the two fluids was cooled to  $-10^\circ \text{C.}$ , and mixed with an excess of a saturated solution of anhydrous sulphuric acid in Nordhausen acid. After standing for several hours, and being repeatedly shaken, no diminution in the volume of the ethereal fluid seemed to have taken place; but on distilling the mixture in a water-bath at a gentle heat, about one half only of the clear, colourless liquid floating upon the sulphuric acid distilled over; the remaining portion, which was volatile only at a very high temperature, I have not further examined; it consisted probably of the conjugate sulphuric acid homologous with that produced by the action of anhydrous sulphuric acid upon olefiant gas. The distillate was placed over pieces of caustic potash until every trace of sulphurous acid had been removed. It had now entirely lost the unpleasant smell which it possessed before treatment with sulphuric acid, and emitted a very agreeable odour, resembling chloroform.

Burnt with oxide of copper, 0.1237 grm. yielded 0.3779 grm. car-



bonic acid, and 0.1856 grm. water, numbers which exactly correspond with the formula  $C_5 H_6$ .

		Calculated.	Found.
$C_5$	.	30	83.33
$H_6$	.	6	16.67
		<hr/>	<hr/>
		36	100.00
			<hr/>
			99.99

A determination of the specific gravity of its vapour gave the following result :

Weight of liquid employed	.	.	0.0863 grm.
Observed vol. of vapour	.	.	39.8 cub. c.
Temperature	.	.	100° C.
Height of barometer	.	.	733.8 <sup>mm</sup>
Difference of mercury level	.	.	31.0 <sup>mm</sup>
Specific gravity of vapour	.	.	2.4657

This result shows that the body in question contains  $2\frac{1}{2}$  vols. carbon vapour, and 6 vols. hydrogen condensed to 1 vol.; for on this supposition, the specific gravity ought to be 2.4876, a number which closely corresponds with that found.

The composition of the body absorbed by sulphuric acid is also determined by the foregoing experiments, which prove that it has a constitution homologous with olefiant gas, but an atomic weight  $2\frac{1}{2}$  times greater; for, according to the vapour analysis, 100 vols. consisted of :

Vapour absorbed by $SO_3$	.	46.78
Vapour not absorbed by $SO_3$	.	53.22
		<hr/>
		100.00

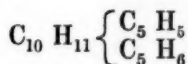
or by weight :

Vapour absorbable by $SO_3$	.	46.08
Vapour unabsorbable by $SO_3$	.	53.92
		<hr/>
		100.00

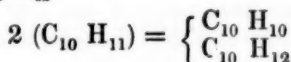
If then, from the results of the combustion of the mixed liquids by oxide of copper (page 34); the weight of carbon and hydrogen corresponding to 53.92 per cent of the body  $C_5 H_6$  be deducted, the remaining numbers give the proportion by volume  $C : H = 1 : 2.10$ , which corresponds sufficiently near with the voluminal proportion  $C : H = 1 : 2$ , when we consider how difficult it is to preserve the

constant composition of a mixture of two such volatile fluids as those in question, during a series of experiments in which the vessel containing them has frequently to be unstopped.

With reference to the true constitution of the two bodies last described, two views may be taken; for they may be regarded either as products of the splitting of 1 eq. amyl into 1 eq.  $C_5 H_5$  and 1 eq.  $C_5 H_6$ .



or as resulting from the transformation of 2 eq. amyl into 1 eq.  $C_{10} H_{10}$  and 1 eq.  $C_{10} H_{12}$



Before giving preference to either of these views, it appeared of importance, first to ascertain whether iodide of amyl, in presence of zinc and water, undergoes a decomposition analogous to that of iodide of ethyl under similar circumstances, and if so, whether the resulting carbo-hydrogen is identical with the body  $C_5 H_6$  or  $C_{10} H_{12}$  just described. I therefore submitted iodide of amyl, mixed with rather more than an equal volume of water, to the action of zinc in an apparatus similar to that already described. In this case, the zinc was not previously amalgamated, as it was found that the unamalgamated metal effected the decomposition with great rapidity at a moderate temperature (about  $140^\circ C$ ). As soon as the action appeared complete, the tube was allowed to cool, and after being cut off at the drawn-out extremity, was connected with a well-cooled receiver, and then partially immersed in a water-bath heated to about  $60^\circ C$ . The colourless, limpid, ethereal fluid, which rapidly distilled over in considerable quantity, was placed over pieces of fused potash for twenty-four hours, and then rectified in a water-bath at  $35^\circ C$ . The residue remaining in the decomposition tube consisted of oxy-iodide of zinc, water, and a trace of undecomposed iodide of amyl.

Burnt with oxide of copper, 0.1813 grm. of the ethereal fluid gave 0.5540 grm. carbonic acid, and 0.2702 grm. water, corresponding to the following per centage composition, and the empirical formula  $C_5 H_6$ .

	Calculated.		Found.
$C_5$ . . .	30	83.33	83.34
$H_6$ . . .	6	16.67	16.56
	<hr/> 36	<hr/> 100.00	<hr/> 99.90

A determination of the specific gravity of its vapour gave the following numbers :

Weight of liquid employed	. . .	0.0965 grms.
Observed vol. of vapour	. . .	44.3 cbc.
Temperature	. . .	100° C.
Height of barometer	. . .	758.4 <sup>mm</sup>
Difference of mercury level	. . .	62.0 <sup>mm</sup>
Specific gravity of vapour	. . .	2.4998

That this body is perfectly identical with that formed during the decomposition of iodide of amyl by zinc, *without* the presence of water, and to which we have assigned the empirical formula  $C_5 H_6$ , the following comparison of their chemical and physical properties, proves beyond all doubt.

Body produced in the decomposition of iodide of amyl by zinc *without* the presence of water.

Results of combustion with oxide of copper.

Carbon . . . 83.32

Hydrogen . . . 16.67

---

99.99

Specific gravity of liquid.

0.6385 at 14.2° C.

Specific gravity of vapour.

2.4657

Boiling point.

30° C. at 734<sup>mm</sup> pressure.

Body produced in the decomposition of iodide of amyl by zinc *with* the presence of water.

Results of combustion with oxide of copper.

Carbon . . . 83.34

Hydrogen . . . 16.56

---

99.90

Specific gravity of liquid.

0.6413 at 11.2° C.

Specific gravity of vapour.

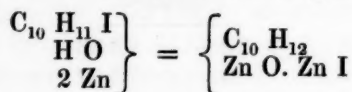
2.4998

Boiling point.

30° C. at 758<sup>mm</sup> pressure.

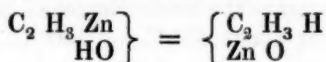
Further, both bodies are equally unacted upon by fuming sulphuric acid, and only with great difficulty by the most powerful oxidizing menstrua; they both possess the same odour, and are perfectly similar in every respect.

The decomposition of iodide of amyl by zinc in presence of water, is perfectly analogous to that of iodide of ethyl under similar circumstances, and may be expressed by the following simple equation :

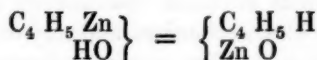


When we consider the above facts in connection with the existence,

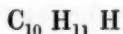
and products of decomposition of zinc-methyl and zinc-ethyl, in which the zinc is so evidently replaced by hydrogen,



and



there can scarcely be a doubt that the rational constitution of the body in question is



and I therefore propose for it the name :

#### HYDRURET OF AMYL.

Hydruret of amyl is a transparent, colourless, and exceedingly mobile fluid, possessing an agreeable odour resembling chloroform. It is insoluble in water, but soluble in alcohol and ether, from the former of which it is again separated by the addition of water : it is the lightest liquid known, its specific gravity being only 0.6385 at 14.2° C. Hydruret of amyl retains its fluidity at — 24° C. ; it boils at 30° C. ; its vapour is easily inflammable, and burns with a brilliant white flame ; placed in a glass flask, having its neck drawn out to a fine orifice, and held in the hand, a constant jet of gas issues, which, on being ignited, gives a pure white light of surpassing brilliancy and devoid of smoke, until the enclosed fluid is entirely evaporated. In accordance with two determinations of the specific gravity of its vapour, it contains 1 vol. amyl vapour and 1 vol. hydrogen united without condensation, or 5 vols. carbon vapour and 12 vols. hydrogen condensed to 2 vols. :

5 vols. Carbon vapour . . . .	4.1461
12 vols. Hydrogen . . . .	0.8292
	<hr/>
2 vols. Hydruret of Amyl . . . .	4.9753
1 vol. of which therefore weighs $\frac{4.9753}{2}$	= 2.4876
Found by experiment { No. I. .	24.657
{ No. II. .	24.998

Hydruret of amyl is not in the least affected by prolonged contact with fuming sulphuric acid ; it is a remarkably stable compound, and is only acted upon with great difficulty by the most powerful reagents.

A determination of the specific gravity of its vapour gave the following numbers :

Weight of liquid employed	. . .	0.0965 grms.
Observed vol. of vapour	. . .	44.3 cbc.
Temperature	. . .	100° C.
Height of barometer	. . .	758.4 <sup>mm</sup>
Difference of mercury level	. . .	62.0 <sup>mm</sup>
Specific gravity of vapour	. . .	2.4998

That this body is perfectly identical with that formed during the decomposition of iodide of amyl by zinc, *without* the presence of water, and to which we have assigned the empirical formula  $C_5H_6$ , the following comparison of their chemical and physical properties, proves beyond all doubt.

Body produced in the decomposition of iodide of amyl by zinc *without* the presence of water.

Results of combustion with oxide of copper.

Carbon . . . 83.32

Hydrogen . . 16.67

---

99.99

Specific gravity of liquid.

0.6385 at 14.2° C.

Specific gravity of vapour.

2.4657

Boiling point.

30° C. at 734<sup>mm</sup> pressure.

Body produced in the decomposition of iodide of amyl by zinc *with* the presence of water.

Results of combustion with oxide of copper.

Carbon . . . 83.34

Hydrogen . . 16.56

---

99.90

Specific gravity of liquid.

0.6413 at 11.2° C.

Specific gravity of vapour.

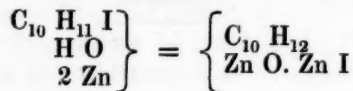
2.4998

Boiling point.

30° C. at 758<sup>mm</sup> pressure.

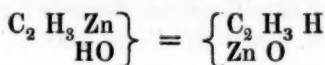
Further, both bodies are equally unacted upon by fuming sulphuric acid, and only with great difficulty by the most powerful oxidizing menstrua; they both possess the same odour, and are perfectly similar in every respect.

The decomposition of iodide of amyl by zinc in presence of water, is perfectly analogous to that of iodide of ethyl under similar circumstances, and may be expressed by the following simple equation :

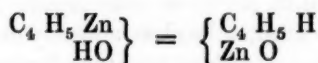


When we consider the above facts in connection with the existence,

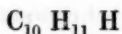
and products of decomposition of zinc-methyl and zinc-ethyl, in which the zinc is so evidently replaced by hydrogen,



and



there can scarcely be a doubt that the rational constitution of the body in question is



and I therefore propose for it the name :

#### HYDRURET OF AMYL.

Hydruret of amyl is a transparent, colourless, and exceedingly mobile fluid, possessing an agreeable odour resembling chloroform. It is insoluble in water, but soluble in alcohol and ether, from the former of which it is again separated by the addition of water : it is the lightest liquid known, its specific gravity being only 0.6385 at 14.2° C. Hydruret of amyl retains its fluidity at — 24° C. ; it boils at 30° C. ; its vapour is easily inflammable, and burns with a brilliant white flame ; placed in a glass flask, having its neck drawn out to a fine orifice, and held in the hand, a constant jet of gas issues, which, on being ignited, gives a pure white light of surpassing brilliancy and devoid of smoke, until the enclosed fluid is entirely evaporated. In accordance with two determinations of the specific gravity of its vapour, it contains 1 vol. amyl vapour and 1 vol. hydrogen united without condensation, or 5 vols. carbon vapour and 12 vols. hydrogen condensed to 2 vols. :

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1 vol. of which therefore weighs $\frac{4.9753}{2}$	= 2.4876
Found by experiment { No. I. . . . .	24.657
{ No. II. . . . .	24.998

Hydruret of amyl is not in the least affected by prolonged contact with fuming sulphuric acid ; it is a remarkably stable compound, and is only acted upon with great difficulty by the most powerful reagents.

It can scarcely be doubted, that this body was present in the liquid obtained by Reichenbach\* in acting upon wood-tar with sulphuric acid, and to which he gave the name *Eupione*: as the boiling point of this liquid varied from about  $47^{\circ}$  C. to  $260^{\circ}$  C., it was evidently a mixture of several compounds. Reichenbach says that the most volatile portion boiled at  $47^{\circ}$  C. or even lower; had a specific gravity 8.633; and formed a clear, colourless, and very mobile fluid, of a somewhat agreeable odour, resembling narcissus flowers: he states that the formula is either  $C_n H_n$ , or some multiple of this, or else one nearly approaching to such a multiple, as  $C_5 H_6$ . It is highly probable that the liquids described by Reichenbach under the name of eupione consisted of a whole series of bodies having the form  $C_n H_{(n+2)}$ , and differing from each other by  $C_2 H_2$ , commencing with hydruret of amyl, and terminating with the hydrurets of the radicals of the wax-alcohols described by Brodie;† and as the gases evolved by the destructive distillation of wood and of coal are already known to contain hydruret of methyl (light carburetted hydrogen), there can be little doubt that the other members of the series intermediate between this last body and hydruret of amyl will also be found in them viz.:

Hydruret of ethyl	.	.	.	.	$C_4 H_5, H$
„ „ butyl	.	.	.	.	$C_6 H_7, H$
„ „ valyl	.	.	.	.	$C_8 H_9, H$

Probably the illuminating power of coal gas depends, to a great extent, upon the presence of these bodies, especially the hydrurets of butyl and valyl.

That the methods hitherto employed in the analysis of coal-gas, have not led to the discovery of these bodies, will cease to create surprise, when we consider that they are probably all unacted upon by fuming sulphuric acid and perchloride of antimony, and that 1 vol. hydrogen with 1 vol. hydruret of ethyl, 2 vols. hydrogen with 1 vol. hydruret of butyl, and 3 vols. hydrogen with 1 vol. hydruret of valyl, give mixtures, all of which have the same specific gravity as hydruret of methyl (light carburetted hydrogen), and further, contain in the same volume, the same relative and absolute quantities of carbon and hydrogen, and would therefore yield, on combustion with oxygen, precisely the same eudiometrical results as hydruret of methyl. If, however, coal-gas, after being freed from the bodies of the form  $C_n H_n$  by being passed through fuming sulphuric acid or

\* Schweigger Seidel's Journal LXVIII, 117, and Ann. Pharm. VIII, 217.

† Ann. Ch. Pharm. 71. 144.



perchloride of antimony, were allowed to stream through alcohol, the compounds in question would no doubt be absorbed, and could be afterwards separated in the gaseous form by the addition of water or by ebullition.

The careful examination of wood and coal tars in connection with the gases evolved during their formation, would certainly lead to highly interesting results, as is indeed already rendered evident by Mansfield's late discovery of large quantities of hydruret of phenyl (benzole) in coal-tar naphtha. The great difficulty attending such investigations has hitherto consisted chiefly in the impossibility of separating the mixed hydrocarbons by fractional distillation. The cause of this difficulty and its remedy seem to be indicated by the foregoing experiments, taken in connection with the boiling points of ethyl, butyrene ( $C_8 H_8$ ), and the amylene of Cahours; for taking the formulæ expressing equal volumes of vapour, we have the following series :

	Formulæ for equal vols. of vapour.	Boiling points.	Differences.
Butyrene ( $C_8 H_8$ ) . . .	$C_4 H_4$	— 17·8° C. }	5·2° C.
Ethyl . . . . .	$C_4 H_6$	— 23·0° „ }	
Valerene* ( $C_{10} H_{10}$ ) . . .	$C_5 H_5$	35·0° „ }	5·0° „
Hydruret of amyl ( $C_{10} H_{12}$ ) . .	$C_5 H_6$	30·0° „ }	
Amylene ( $C_{20} H_{20}$ ) . . .	$C_{10} H_{10}$	160·0° „ }	5·0° „
Amyl . . . . .	$C_{10} H_{11}$	155·0° „ }	

Thus it appears, that a carbo-hydrogen having the formula  $C_n H_n$ , and its companion  $C_n H_{(n+1)}$  differ in their boiling points by only 5° C., or in other words, the addition of 1 eq. hydrogen, without increase in the volume of vapour, depresses the boiling point 5° C., thus rendering the separation of two such bodies by distillation alone impossible; but by the employment of anhydrous sulphuric acid, all the compounds having the form  $C_n H_n$  would, in all probability be removed, and as the bodies  $C_n H_{(n+1)}$  and  $C_{(n+2)} H_{(n+3)}$ , lying next to each other in the remaining series, have boiling points differing, so far as is yet known, by at least 47° C., their separation by fractional distillation could be easily effected.

Further, it is not impossible, that by regulating the temperature at which the destructive distillation of wood and coal is carried on, considerable quantities of hydruret of amyl might be cheaply obtained, which, as illuminating material, would surpass almost every other in convenience and brilliancy.

\* The body produced from amyl simultaneously with hydruret of amyl. (See below.)

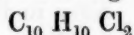
## VALERENE.

The same reasons which led me to adopt the formula  $C_{10}H_{11}H$  for one of the products of the transformation of amyl, point also to  $C_{10}H_{10}$  as the rational formula of the second; for, if from 2 eq. amyl, 1 eq. hydruret of amyl be deducted, the elements  $C_{10}H_{10}$  remain, and fill a vacant space in the olefiant gas series.

$$\begin{array}{rcl}
 2 \text{ eq. Amyl} & . & . & . & = & C_{20}H_{22} \\
 1 \text{ eq. Hydruret of amyl} & = & C_{10}H_{12} \\
 \hline
 1 \text{ eq. Valerene} & . & . & . & = & C_{10}H_{10}
 \end{array}$$

Our knowledge of the rational constitution of the whole series of bodies having the formula  $C_nH_n$  in which  $n$  is an even number, is much too limited to allow of permanent names being given to any of them. I have named the body under consideration, *Valerene*, in accordance with the names given to the other known members of the same series; but without any reference whatever to its true constitution.

Valerene is a colourless and transparent liquid possessed of a peculiar penetrating and disagreeable odour much resembling butyrene ( $C_8H_8$ ), so far as these properties can be judged of from its mixture with hydruret of amyl. Its boiling point is about  $35^\circ$  C. It is rapidly and perfectly absorbed by anhydrous sulphuric acid and by perchloride of antimony, with which last it no doubt forms the compound analogous to the oil of olefiant gas :



On the supposition that it contains 5 vols. carbon vapour, and 10 vols. hydrogen condensed to 2 vols., the specific gravity of its vapour would be 2.41855.

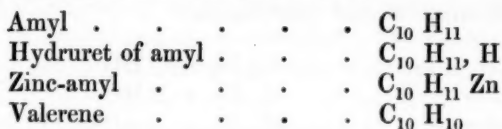
$$\begin{array}{rcl}
 5 \text{ vols. Carbon vapour} & . & . & 4.1461 \\
 10 \text{ „ Hydrogen} & . & . & 0.6910 \\
 & & & \hline
 2 \text{ „ Valerene vapour} & . & . & 4.8371 \\
 1 \text{ vol. of which therefore weighs} & \frac{4.8371}{2} & = & 2.41855
 \end{array}$$

The specific gravity, as calculated from that of the mixture of valerene and hydruret of amyl, is 2.3863, which agrees sufficiently well with the theoretical number. I have not studied its properties further.

In addition to the bodies above-described, iodide of amyl when decomposed by zinc, yields zinc-amyl, a body having properties quite

analogous to those of zinc-ethyl and zinc-methyl. The complete history of these compounds will be given in a future communication.

The foregoing experiments show that the decomposition of iodide of amyl by zinc gives rise to four new bodies, viz. :



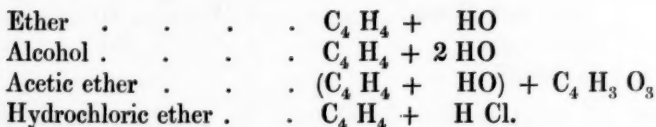
Iodide of amyl is also decomposed by potassium with great rapidity, when the fluid is heated to the fusing point of the metal; the results of the decomposition are precisely the same as those obtained by zinc, except that no compound containing potassium analogous to zinc-amyl is formed. This process cannot however be conveniently employed for the preparation of amyl, because the iodide of potassium assumes such a bulky form as to render necessary the distillation of the fluids from this salt at least five or six times, before the decomposition can be completed, which is attended with great loss.

Perhaps no class of compounds within the whole range of chemistry has been so closely investigated, and at the same time the subject of such difference of opinion, as the bodies termed alcohols, and their derivatives, the ethers; the well-marked properties and reactions of the whole series, so far as its individual members are known, and the theoretical as well as practical interest connected with the subject, make the development of the true constitution of these compounds one of the most important problems of chemical science.

Gay-Lussac was the first to throw out a suggestion upon the possible rational composition of alcohol and ether, which he hinted might be regarded as compounds of olefiant gas and water, but still preferred to view them as ternary compounds of carbon, hydrogen and oxygen. The former view was soon after taken up by Dumas and Boullay,\* and worked out into their well known theory, in which they assume alcohol and ether to be hydrates of olefiant gas, the oxalic, acetic, &c., ethers, as compounds of the first hydrate of that body with the respective oxygen acids, and the ethereal bodies formed by the hydrogen acids, as compounds of these acids with olefiant gas. This hypothesis was principally borne out by the then received views

\* Ann. Chim. Phys. LXX, 95.

of the constitution of sulphovinic acid and oxamide, together with the belief, then prevalent, that sulphuric acid, by the absorption of olefiant gas, was converted into sulphovinic acid. Dumas and Boullay regarded ether, alcohol, acetic and hydrochloric ethers, as having the following rational constitution :



The subsequent development of the true constitution of oxamide and sulphovinic acid, abstracting as they did the principal support of this theory, led to the views of Kane, Berzelius and Liebig being very generally adopted, at least in England and Germany. Berzelius\* proposed to regard ether as the oxide of a compound radical, ethyl ( $C_4 H_5$ ),† and alcohol as the oxide of the radical ( $C_2 H_3$ ); in this view, so far as ether is concerned, he was soon after supported by Liebig, who, however, regarded alcohol as the hydrate of the oxide of ethyl; and these views he confirmed and illustrated by his beautiful researches, on the constitution of the oxamide‡ procured by the action of ammonia on oxalic ether, and on the process of etherification,|| which led him to the following conclusions :§

1. "That the views of Dumas and Boullay on the constitution of ether, according to which this body is the hydrate of olefiant gas, are not supported by any single fact."

2. "That the only consistent view, which is contradicted by no fact, but which, on the contrary, satisfactorily explains all phenomena connected with its compounds, consists in regarding ether as the protoxide of a compound radical,  $C_4 H_5. O$ ."

The same chemist adds further, "I have no doubt that the radical of ether, viz., the carbo-hydrogen,  $C_4 H_5$ —will be obtained free from every other body."

The isolation of four of the compound radicals belonging to the alcohol series, now excludes every doubt of their actual existence, and furnishes a complete and satisfactory proof of the correctness of the

\* Pogg. Ann. XXVIII, 626; and Annual Report, presented to the Academy of Sciences, at Stockholm, March 31st, 1833.

† Kane was the first to regard ether as the protoxide of a compound radical  $C_4 H_5$ , which he named *Ethereum* (Dub. Jour. of Med. Science, Jan. 1833).

‡ Ann. Chem. Pharm. IX, 6, 129.

|| Idem. XXX, 129; XXIII, 12.

§ Idem. IX, 15.

theory propounded by Kane, Berzelius and Liebig fifteen years ago. The radicals already known in their free state—viz. : methyl, ethyl, valyl, and amyl—are sufficient to enable us to judge of the chemical relations of the whole series. As might have been predicted from their behaviour in combination, they present in their free state the closest relations to hydrogen and the noble metals; like these elements they are, when uncombined, almost perfectly indifferent, and withstand the most powerful oxidizing influences, whilst in *statu nascenti* they readily pass from one state of combination to another, and the constitution of the vapours of these compounds is always perfectly analogous to that of the corresponding compounds of the simple radical hydrogen; the following examples may suffice as illustrations :

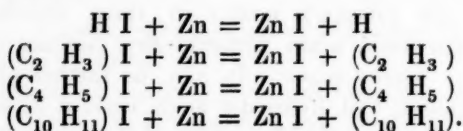
1 vol. hydrogen combines with $\frac{1}{2}$ vol. oxygen, and forms 1 vol. watery vapour.	
1 " methyl " " $\frac{1}{2}$ " " " 1 " oxide of methyl.	
1 " ethyl " " $\frac{1}{2}$ " " " 1 " ether vapour.	
1 " amyl " " $\frac{1}{2}$ " " " 1 " oxide of amyl vapour.	

1 vol. H combines with 1 vol. Cl, and forms 2 vols.	H	Cl
1 " C <sub>2</sub> H <sub>5</sub> " " 1 " Cl " " 2 " C <sub>2</sub> H <sub>5</sub> Cl		
1 " C <sub>4</sub> H <sub>9</sub> " " 1 " Cl " " 2 " C <sub>4</sub> H <sub>9</sub> Cl		
1 " C <sub>10</sub> H <sub>21</sub> " " 1 " Cl " " 2 " C <sub>10</sub> H <sub>21</sub> Cl		

The compounds of bromine, iodine, fluorine, and cyanogen, are also perfectly analogous to the above: indeed, so complete is the homology of the compound radicals, methyl, ethyl and amyl, with hydrogen, that even their haloid compounds present the closest relations to hydracids, as is strikingly exemplified in the behaviour of their iodides: for, although these bodies do not possess the property of reddening litmus-paper, yet this is probably owing to the insolubility of the colouring matter in these liquids; for even hydriodic acid gas itself, when perfectly dry, has not the slightest action upon dry litmus paper. It may be further objected, that aqueous hydrochloric and hydriodic acids rapidly dissolve zinc at ordinary temperatures, whilst the iodides of methyl, ethyl, &c., have no action upon that metal, until aided by heat. To ascertain how far this objection is well-grounded, I allowed dry hydrochloric acid gas to stream over commercial zinc, freshly granulated; not the slightest action took place, the brilliant surface of the metal remained untarnished, and the escaping gas was perfectly absorbed by water, until the temperature of the zinc was raised to about 100° C.; and even then, the decomposition of the acid gas was only very partial, and ceased almost entirely as soon as the surface of the zinc became covered with chloride, although the temperature was raised until the metal fused into globules. This experiment proves that even hydro-

chloric acid itself, when free from water, is acted upon by zinc only when aided by heat, and even then with difficulty. The facility with which the series of bodies, beginning with hydriodic acid and terminating with iodide of amyl, are decomposed by zinc, appears to be inversely as the atomic weight of the electro-positive group,—or in other words, the electro-negative character of the compound decreases as the atomic weight increases; for hydriodic acid is decomposed at 100° C., iodide of methyl at 150° C., iodide of ethyl with more difficulty between 150° and 160° C., and iodide of amyl with very great difficulty at 190° C. The cause of this phenomenon probably lies to some extent in the more difficult solubility of the iodide of zinc in the surrounding liquid, as the latter approaches more nearly to the character of an oil. Further, hydriodic acid is rapidly decomposed, with separation of free iodine, under the simultaneous influence of atmospheric air and faint diffused daylight; iodide of methyl presents the same phenomenon, but requires to be exposed to these influences for a much longer time; iodide of ethyl, placed under similar circumstances, side by side with the last, did not exhibit a trace of colour at the end of four months, but when exposed to stronger diffused light, became brown, from separation of free iodine, in a few hours; whilst iodide of amyl, exposed to strong daylight for a much longer time, did not exhibit any trace of colour, and only does so, according to Cahours, when exposed to direct sunlight.

The decomposition of these iodine compounds, and of hydriodic acid, by zinc, gives perfectly analogous results, as is seen from the following equations :



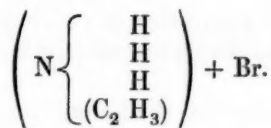
Again, the late beautiful researches of Hofmann on the Organic Bases,\* appear to me to confirm the claims of the haloid compounds of these radicals to the character of hydracids, in a most remarkable manner, and at the same time verify the suggestion I threw out in a former memoir,† that these radicals would be found capable of replacing hydrogen in many of the combinations of that element; for Hofmann has shewn that these compounds combine with ammonia, aniline, &c., with an energy inferior only to that of the

\* Ann. Ch. Pharm. LXXIII, 91.

† Chem. Soc. Qu. J. II, 299.



corresponding hydracids themselves. The most simple explanation of these reactions, and one which at the same time satisfactorily explains every fact connected with them, appears to me to consist in regarding the ethereal body as playing the part of a hydracid. Although the subsequent decomposition, by potash, of the salts thus formed seems at first sight to militate against this view, yet, I conceive, a little closer attention to the nature of the compound formed, and to the *modus operandi* of the alkali, completely sets this difficulty aside; for if we grant the existence of ammonium, we must also admit that when hydrochloric acid combines with ammoniacal gas, the chlorine in the former remains no longer united with any single atom of hydrogen, but on the contrary, with the group  $(\text{N H}_4)$ ; so also, when ammoniacal gas unites with bromide of methyl, the bromine remains no longer in combination with the methyl, but is united with the whole group—with ammonium, in which 1 eq. of hydrogen has been replaced by methyl:



The action of potash upon such a compound could easily be predicted; for, as the bromine is not in combination with any particular atom of hydrogen or methyl, and as the alkali has a much stronger affinity for hydrobromic acid than for the bromide of methyl, the nature of the decomposition is thereby determined, and the products are bromide of potassium, water, and the new base,—which last, by being again treated with bromide of methyl, has, by a precisely similar process, the remaining atoms of hydrogen replaced by methyl.

The replacement of hydrogen by methyl is also strikingly exemplified in Paul Thénard's\* new bases containing phosphorus, which, although that chemist regards them as otherwise constituted, are evidently nothing else but the three phosphuretted hydrogens, in which the hydrogen has been replaced by methyl; for, as phosphide of calcium, in contact with hydrochloric acid gives rise to the three compounds of phosphorus and hydrogen,  $\text{P H}_3$ ,  $\text{P H}_2$ , and  $\text{P}_2 \text{ H}$ , so, by substituting chloride of methyl for the hydracid, the corresponding compounds of this radical are produced. According to this view, the rational constitution of these compounds, and their

\* Compt. Rend. XXV, 892.

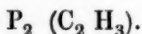
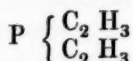
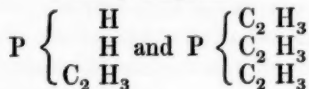


complete correspondence with the three phosphuretted hydrogens, may be thus expressed :

Hydrogen compounds.



Methyl compounds.



As P. Thénard mentions that he has also obtained a similar series containing ethyl, there can be little doubt that another containing amyl will also be formed. The remarkable relation of these bodies to ammonia, and to the bases of Hofmann and Wurtz, cannot be overlooked. It would be interesting to ascertain whether or not the phosphuretted hydrogens themselves are possessed of basic qualities. Indeed, Rose has already shown that one of them ( $P H_3$ ) bears a close relation to ammonia, and forms several salts isomorphous with those of that base.

The remarkable property of combining with hydrogen to form hydrurets, which seems to be possessed by the radicals of the series to which methyl, ethyl, &c., belong, and which appears to be participated in by the allied series, beginning with phenyl, leads to a very simple view of the constitution of a number of compounds, whose rational formulæ have hitherto been considered doubtful :

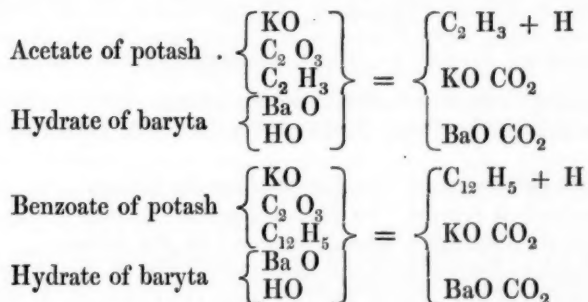
Light carburetted hydrogen . . . . .	$C_2 H_3 + H =$	hydruret of methyl.*
The gas formed by the action of water upon zinc-ethyl, and by the transformation of ethyl into $C_4 H_4$ , and $C_4 H_5$ , H . . . . .	$C_4 H_5 + H =$	„ „ ethyl.†
Volatile liquid described above . . . . .	$C_{10} H_{11} + H =$	„ „ amyl.
Phenol (benzole) . . . . .	$C_{12} H_5 + H =$	„ „ phenyl.
Toluol . . . . .	$C_{14} H_7 + H =$	„ „ toluyl.
Cumol . . . . .	$C_{18} H_{11} + H =$	„ „ cumyl.
Cymol . . . . .	$C_{20} H_{13} + H =$	„ „ cymyl.

The action of chlorine upon the so-called methyl from cyanide of ethyl, increases still further the probability of this hypothesis, whilst the formation of nitro-compounds of phenol, toluol, &c. (by the

\* Kolbe has already proposed this as the rational formula of light carburetted hydrogen. See "*Handwörterbuch der Chemie*, art. *Grubengas*."

† It is highly probable that the so-called methyl gas, generated by the decomposition of cyanide of ethyl by potassium, is also hydruret of ethyl, and therefore only isomeric with the true radical methyl produced in the electrolysis of acetic acid, and in the decomposition of iodide of methyl by zinc.

replacement of 1 eq. of hydrogen by  $\text{NO}_4$ ), yielding, on reduction with sulphuretted hydrogen, the bases aniline, toluidine, &c., taken in connection with the true constitution of these bases, recently so completely and satisfactorily demonstrated by Hofmann, gives additional weight to the evidence in favour of this view, which also explains the production of light carburetted hydrogen and phenol, by the dry distillation, respectively, of acetate and benzoate of potash with hydrate of baryta, in the most simple and satisfactory manner :



I am at present engaged with some experiments to ascertain whether the dry distillation of the salts of metacetic, butyric and valerianic acids, with hydrate of baryta, will not yield, in the same manner respectively, the hydrurets of the radicals, ethyl, butyl and valyl; and the results of these experiments I hope to lay before the Society at an early period.

The conclusions to which the foregoing remarks lead may be briefly expressed as follows :

1. That the radicals of the series to which methyl, ethyl, amyl, &c., belong, possess exactly the chemical relations and character of hydrogen, than which they are, however, less electro-positive.

2. That these radicals can replace hydrogen in every combination in which that element plays the part of a simple radical, and is not enclosed in a group acting the part of a compound radical.

3. That the haloïd compounds of these bodies may be regarded as hydracids, in which hydrogen is replaced by one of these radicals; and the organic acids of the series,  $(\text{CH})_n + \text{O}_4$ , as formic acid, in which the conjugate atom of hydrogen is replaced in the same manner.

4. That the replacement of hydrogen in ammonia by these radicals, as exemplified in the bases of Hofmann and Wurtz, renders the assumption of the hypothetical radical amidogen, superfluous.

5. That these radicals, in addition to the property of combining

with the electro-negative elements, possess also the faculty of uniting with hydrogen to form hydrurets.

To Professor von Liebig, in whose Laboratory the foregoing investigation was made, I take this opportunity of returning my warmest thanks for his advice and extreme kindness in affording me every facility for the execution of the requisite experiments.

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March 4, 1850.

ROBERT PORRETT, Esq., Treasurer, in the Chair.

The following Presents were laid upon the table :

"Transactions of the Royal Society," for 1848—9, presented by the Society.

"Philosophical Magazine," for March, from the Editor.

"Pharmaceutical Journal," for March, from the Editor.

Regnault's "Traité de Chimie," presented by the Author.

"Miscellaneous Results from the Laboratory," and on the "Composition of Linseed-oil Cake," by J. T. Way (from the Quarterly Agricultural Journal), both presented by the Author.

The following Paper was read :

IX.—*Notice of Observations on the adjustment of the relations between the Animal and Vegetable Kingdoms, by which the vital functions of both are permanently maintained.*

By ROBERT WARINGTON, F.C.S.

This communication will consist of a detail of an experimental investigation, which has been carried on for nearly the last twelve months, and which appears to illustrate, in a marked degree, that beautiful and wonderful provision which we see every where displayed throughout the animal and vegetable kingdoms, whereby their continued existence and stability are so admirably sustained, and by which they are made mutually to subserve, each for the other's nutriment, and even for its indispensable wants and vital existence. The experiment has reference to the healthy life of fish preserved in a limited and confined portion of water. It was commenced in May, 1849, and the subjects chosen were two small gold-fish. These were placed in a large glass receiver of about twelve gallons capacity, having a cover of thin muslin stretched over a stout copper wire, bent into a circle, placed over its mouth, so as to exclude, as much as possible, the sooty dust of the London atmosphere, without, at the same time, impeding the free passage of the atmospheric air. This receiver was

about half filled with ordinary spring water, and supplied at the bottom with sand and mud, together with loose stones of larger size of limestone tufa, from the neighbourhood of Matlock, and sandstone; these were arranged so that the fish could get below them, if they wished so to do. At the same time that the fish were placed in this miniature pond, if I may so term it, a small plant of the *Vallisneria spiralis* was introduced, its roots being inserted in the mud and sand, and covered by one of the loose stones, so as to retain the plant in its position. The *Vallisneria spiralis* is one of those delicate aquatic plants generally selected by the microscopist for the exhibition of the circulation of the sap in plants. It throws out an abundance of long, wiry, strap-like leaves, of about  $\frac{1}{4}$  inch in breadth, and from 1 to 3 feet in length; these leaves, when the sun shines on them, evolve a continued stream of oxygen gas, which rises in a current of minute bubbles, particularly from any part of the leaf which may have received an injury.

The materials being thus arranged, all appeared to go on well for a short time, until circumstances occurred which indicated that another and very material agent was required to perfect the adjustment, and which, from my not having thought of at the time of commencing the experiment, had not been provided against. The circumstances I allude to arose from the internal decay of the leaves of the *Vallisneria*, which became yellow from having lost their vitality, and began to decompose; this, by accumulation, rendered the water turbid, and caused a growth of mucus, or green, slimy matter on the surface of the water, and on the sides of the receiver. If this had been allowed to increase, I conceive that the healthy life of the fish must have suffered, and probably their vital functions have been destroyed. The removal of these decaying leaves from the water, therefore, became a point of permanent importance to the success of the experiment. To effect this, I had recourse to a very useful little scavenger, whose beneficial functions have been too much overlooked in the economy of animal life,—I mean the water-snail, whose natural food is the very green, slimy growth, or mucus and decaying vegetable matter, which threatened to destroy the object which was wished to be obtained. Five or six of these creatures—the *Himnæa stagnalis*—were consequently introduced, and, by their continued and rapid locomotion and extraordinary voracity, soon removed the cause of interference, and restored the whole to a healthy state, thus perfecting the balance between the animal and vegetable inhabitants, and enabling both to perform their vital functions with health and energy.

So luxuriant was the growth of the *Vallisneria* under these circumstances, that, by the autumn, the one solitary plant that had been originally introduced; had thrown out myriads of off-shoots and suckers, thus multiplying to the extent of upwards of thirty fine, strong plants; and these threw up their long, spiral, flowering stems in all directions, so that, at one time, more than forty blossoms were counted lying on the surface of the water.

The fish have been lively, bright in colour, and appear very healthy, and the snails also—judging from the enormous quantity of gelatinous masses of eggs which they have deposited on all parts of the receiver, as well as on the fragments of stone—appear to thrive wonderfully, and, besides their functions in sustaining the perfect adjustment of the series, afford a large quantity of food to the fish in the form of the young snails, which are devoured as soon as they exhibit signs of vitality and locomotion, and before their shell has become hardened.

Thus we have that admirable balance sustained between the animal and vegetable kingdoms, and that in a liquid element. The fish, in its respiration, consumes the oxygen held in solution by the water as atmospheric air; furnishes carbonic acid; feeds on the insects and young snails; and excretes material well adapted as a rich food to the plant, and well fitted for its luxuriant growth.

The plant, by its respiration, consumes the carbonic acid produced by the fish, appropriating the carbon to the construction of its tissues and fibre, and liberates the oxygen in its gaseous state to sustain the healthy functions of the animal life, at the same time that it feeds on the rejected matter, which has fulfilled its purposes in the nourishment of the fish and snail, and preserves the water constantly in a clear and healthy condition,—while the slimy snail, finding its proper nutriment in the decomposing vegetable matter and minute confervoid growth, prevents their accumulation by removing them from the field, and, by its vital powers, converts what would otherwise act as poison, into a rich and fruitful nutriment, again to constitute a pabulum for the vegetable growth, while it also acts the important part of a purveyor to its finny neighbours.

March 18, 1850.

J. T. COOPER, Esq., V.P. in the Chair.

Charles Shearman, Esq., John Cameron, Esq., and George Ewbanks, Esq., were elected Fellows of the Society.

The "Quarterly Journal of the Geological Society" was laid on the table, as a donation from the Society.

The following Papers were read :

"On the relations between Chemical Composition, Boiling Point, and Specific Volume," by Professor Hermann Kopp, (to be published in the next number).

X.—*On the Precipitation of the Colouring Matter of Sugar by a Metallic Oxide.* By HENRY WARBURTON, F.R.S. F.G.S., &c.

(In a letter to PROFESSOR GRAHAM).

Allow me to put upon paper what I said to you the other day, respecting the experiments I made many years ago (the year of Mr. Howard's death) with the view of precipitating the colouring matter of brown sugar in combination with a metallic oxide.

My assistant was a gentleman related, by marriage, to Mr. Howard, and his operator in all the experiments on sugar-refining and filtering connected with Mr. Howard's patents. He gave me the information I was in want of, as to the strength of the syrups at which it would be requisite to effect the precipitation of the colouring matter, in order to render any process of that kind available to the sugar refiner. He prepared for me a small apparatus for filtering the syrups at a boiling heat, and pronounced judgment on the results obtained.

The metals I used were iron, lead, zinc, and *tin*. Iron, I at once abandoned. Lead, I was afraid of; though, with the sub-acetate, followed by a little sulphuric acid, and that followed by a little hydrate of lime, I obtained very colourless results.

With the sulphate of zinc, the results were very good. A solution of this salt was first mixed with the syrups, and then hydrate of lime was added, equivalent to the sulphuric acid in the salt. One experiment of this kind was made on the great scale at the boiling-house of a firm with whom Mr. Howard was connected in business, and was regarded by them as highly promising. However, Dr. Wollaston found a trace of zinc in some of the syrups which had been thus treated, and I was afraid of zinc also.



The best results of all were obtained with sulphate of tin; and one experiment, on the large scale, was made with this salt at the boiling-house of the firm referred to. I am sorry that I cannot lay my hand on my cotemporary memoranda of the details of all my experiments with this salt; and you must be content, therefore, with the outline of them, which I now give from memory.

The salt was prepared by precipitating the copper of blue vitriol with grain tin, the latter being finely granulated by crushing it while hot by a wooden pestle; and to prevent the copper from coating the tin as it precipitated, clean copper plates were immersed in the liquid with the tin. Perhaps the best way would be to make the precipitation in a clean copper vessel. To hasten the precipitation, I sometimes added an excess of sulphuric acid; and I kept the vessels cool by immersing them in water. I could not obtain a strong solution of tin in sulphuric acid by the direct action of sulphuric acid on tin: a quantity of subsulphate, or insoluble oxide, in this case, was always found.

After adding a solution of the sulphate of tin to the syrup, a quantity of hydrate of lime, rather more than equivalent to the sulphuric acid, was superadded, and then the syrup was boiled by steam and filtered hot, in a vessel surrounded by steam. I also used, with great success, as a precipitant of the sulphuric acid, freshly precipitated hydrated oxide of lead. But this was only in experiments on the small scale.

Astonishingly perfect results are obtained with the sulphate of tin, when you operate with *dilute syrups*. The difficulty consists in effecting a complete precipitation of the colouring matter in *the syrups of the strength usually employed by the refiner*. Dr. Wollaston did not find any oxide of tin in the syrups treated with tin.

My friend, Dr. Wollaston's relative, always advised the final employment of a small quantity of animal charcoal, as it gave a *fluidity* to strong syrups, that could be obtained in no other way. In our small experiments, we added a *soupeçon* of animal charcoal, after the tin and lime had done their work.

As I made these experiments only for my own amusement, and to serve Mr. Howard's family, if his relatives or the firm thought fit to persevere in them, I left the matter in their hands. But this was the critical period for them, when the refiners were just beginning to take out licenses to boil sugar under Mr. Howard's patents; and their opinion, which appeared to me a well-founded one, was, that any new improvements, suggested at that period, would tend to



unsettle the minds of the refiners, and rather deter them from making up their minds to apply at once for a license.

I conclude that all the tin employed may be recovered, without difficulty, from the precipitate, which will be a mixture of gypsum and vegetable matter combined with oxide of tin. It would be a saleable article to metallurgists; so also will the precipitated copper be.

I shall be curious to know whether any experiments you may make with the sulphate of tin prove satisfactory. Of course, any other soluble salt of tin will answer, when the dissolving acid is neutralized by lime or an alkali, subject to the condition, that the new compound thus found is not soluble in the syrup.

# XI.—On the Composition of the Ashes of the Cactus.

By FREDERICK FIELD, ESQ.

The great abundance of various species of *Cacti* upon all the hills and mountains of Chili, even upon the most barren spots, and in the most arid seasons, led me to investigate the inorganic constituents of this tribe of plants, more especially as in England and most parts of Europe, the Cactus is only known in the conservatories of a few individuals.

Several branches from a plant more than 16 feet in height were carefully cut from the parent stem, and after having been redivided, were exposed to the temperature of 212° Fahr. for the space of fourteen days. 185·00 grs. lost 157·42, leaving 27·58 solid matter, which numbers correspond to :

Water . . .	85·09
Solid matter . .	14·91
	<hr/>
	100·00

29·80 grs. of this solid matter incinerated with every precaution in a platinum crucible, gave 5·00 grs. of ash, equal to 16·79 per cent.

185·00 grs. of recently cut branches (with the thorns or spines attached), gave, on incineration, 2·50 grs. of ash corresponding to 1·35 grs. per cent.

In the following analyses, the soluble and insoluble portions were examined separately, the proportions, for the sake of perspicuity, being reduced to percentage numbers.

## Determination of matter soluble in water :

I.	100 grs. gave	.	.	57·010
II.	100 „ „	.	.	57·300

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Mean 57·155

The composition of this soluble matter is as follows, in 100 parts :

Sulphuric acid	.	.	.	6·232
Chloride of sodium	.	.	.	18·767
Potash	.	.	.	9·873
Soda	.	.	.	35·585
Phosphoric acid	.	.	.	2·265
Carbonic acid	.	.	.	26·046
				<hr/>
				98·768
Loss in analysis	.	.	.	1·232
				<hr/>
				100·000

## Determination of matter insoluble in water :

I.	100 grains gave	.	.	42·842
II.	100 „ „	.	.	42·620

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Mean 42·730

## The composition of this insoluble matter in 100 parts :

Sand and charcoal	.	.	.	2·300
Silicic acid	.	.	.	27·830
Sulphuric acid	.	.	.	1·952
Carbonic acid	.	.	.	25·562
Phosphoric acid	.	.	.	7·806
Phosphate of iron	.	.	.	2·338
Lime	.	.	.	17·925
Magnesia	.	.	.	13·162
Oxide of manganese	.	.	.	0·558
Loss	.	.	.	0·567
				<hr/>
				100·000

Upon adding the soluble and insoluble portions together, and calculating the general composition of the ash, we find in every 100 parts :

## SOLUBLE PORTION :

Sulphuric acid . . . . .	3.561
Chloride of sodium . . . . .	10.726
Potash . . . . .	5.642
Soda . . . . .	20.338
Phosphoric acid . . . . .	1.294
Carbonic acid . . . . .	14.836

## INSOLUBLE PORTION :

Sand and charcoal . . . . .	0.982
Silicic acid . . . . .	11.891
Sulphuric acid . . . . .	0.834
Phosphoric acid . . . . .	3.325
Carbonic acid . . . . .	10.927
Phosphate of iron . . . . .	0.999
Lime . . . . .	7.659
Magnesia . . . . .	5.624
Oxide of manganese . . . . .	0.238
Loss in analysis . . . . .	1.124

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 100.000

As the carbonic acid is doubtless derived from the decomposition of organic acids, and the sand and charcoal may be regarded as accidental, and of no value in the analysis, they may be deducted: we then have the following numbers :

Sulphuric acid . . . . .	6.094
Chloride of sodium . . . . .	14.869
Potash . . . . .	7.832
Soda . . . . .	28.196
Phosphoric acid . . . . .	6.404
Silicic acid . . . . .	16.486
Phosphate of iron . . . . .	1.384
Lime . . . . .	10.649
Magnesia . . . . .	7.747
Oxide of manganese . . . . .	0.339

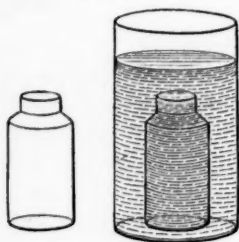
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 100.000

From this it appears that the cactus belongs to the first class, that is to say, to that in which the carbonates of the alkalis and alkaline earths predominate.

XII.—*On the application of Liquid Diffusion to produce Decompositions.* By THOMAS GRAHAM, F.R.S. F.C.S.

The experiments to be described in the sequel of this paper were conducted in the same manner as those contained in a late communication to the Royal Society.\* A set of phials, of nearly equal capacity, were made use of, all cast in the same mould, and further



adjusted by grinding to a uniform size of aperture. The dimensions for a phial (see Fig.) were 3·8 inches in height, with a neck 0·5 inch in depth; aperture 1·25 inch in diameter, and capacity to base of the neck, 2080 grains of water, or between 4 and 5 ounces. For each phial a plain glass jar was also provided, 4 inches in diameter and 7 inches in depth. The method of observing the diffusion of a salt will be

best explained by an example.

For my present object, it was necessary to observe the spontaneous diffusion into pure water of several salts, already dissolved in 100 times their weight of water. The phial was filled with such a solution of sal-ammoniac, for instance, to the base of the neck, or, more correctly, to a distance of exactly 0·5 inch from the ground surface of the lip. The neck of the phial was then filled up with distilled water, a light float being placed on the surface of the solution, and care taken to avoid agitation, after the phial had been placed within the jar. The latter was then filled up with distilled water, so as to cover the open phial to the depth of an inch, which required about twenty ounces of water. The saline liquid in the "solution-phial" is thus allowed to communicate freely with the water of the "water-jar." The water of the latter forms an atmosphere into which salts spread or diffuse, escaping from the solution-phial with different degrees of velocity. The phial and jar together form the "diffusion-cell." The diffusion is interrupted by placing a small plate of ground glass upon the mouth of the phial, and raising the latter out of the jar. The amount of salt diffused, or the "diffusion-product," is learned by evaporating the water of the jar to dryness, or with this and the following chlorides, by precipitating with nitrate of silver.

The diffusion was always allowed to proceed for a period of exactly seven days, unless another time is expressly mentioned. The experiments were conducted in a vault, of which the temperature did not vary more than one degree on either side 50° F.

\* On the Diffusion of Liquids. Read December 21, 1849.

The one per cent solution of sal-ammoniac, in the solution-phial, would contain 20·8 grains of salt. Of this quantity of salt, 3·49 grs. were found to diffuse out into the water-jar in the time mentioned, in one experiment, and 3·36 grains in another experiment. The mean of these two diffusion-products is 3·42 grs., which is, therefore, the quantity of hydrochlorate of ammonia diffused out of the solution-phial, containing a 1 per cent solution of that salt, in a period of seven days.

The diffusion of a 1 per cent solution of chloride of sodium, in similar circumstances, gave, in eight cells, the following products: 3·02, 2·83, 2·86, 2·68, 2·74, 2·70, 2·80 and 2·94 grs., of which the mean is 2·85 grs. These results for the chlorides of ammonium and sodium approach to the theoretical ratio of 1·4142 to 1·7320, that is, of the square root of 2 to the square root of 3.

Anhydrous chloride of calcium gave 2·01 and 2·04 grs. in two experiments; mean 2·02 grs.

Anhydrous chloride of magnesium gave 2·15 and 1·90 grs; mean 2·03 grs. These two earthy chlorides appear, therefore, to be equally diffusible. I may place along with these results, the diffusion-products which the alkaline hydrates, and a few other salts would have afforded in similar circumstances, the latter numbers being deduced from experiments detailed in the paper on the diffusion of liquids already referred to.

SALT DIFFUSED FROM A 1 PER CENT SOLUTION IN EQUAL TIMES.

Hydrate of potash . . . . .	4·84 grs.
„ „ soda . . . . .	4·03 „
Chloride of ammonium . . . . .	3·42 „
„ „ potassium. . . . .	3·42 „
„ „ sodium . . . . .	2·85 „
Sulphate of soda. . . . .	2·35 „
Chloride of calcium . . . . .	2·02 „
„ „ magnesium . . . . .	2·03 „
Sulphate of lime. . . . .	1·21 „
„ „ magnesia . . . . .	1·21 „

The alkaline hydrates have the highest diffusibility, being twice as diffusive as the sulphates of the same bases, and four times as diffusive as the sulphates of magnesia and lime. The salts of potash and ammonia, of the same acid, have an equal diffusibility, which is greater than the diffusibility of the corresponding salts of soda.

Now it has been shown that, when two salts are dissolved together

in the solution-phial, they diffuse independently, each salt maintaining its own rate of diffusion. Hence the possibility of separating salts to a certain extent, by diffusion, in a manner analogous to the separation of substances of unequal volatility by distillation. Further, decompositions may be effected by diffusion, such as the decomposition of alum, the sulphate of potash being separated from the sulphate of alumina, from the higher diffusibility of the former substance.

It appeared probable, also, that, in a mixture of several salts, the acids and bases would have a tendency to arrange themselves so as to form the most diffusive compounds, when an opportunity for diffusion was presented. This would be analogous to the sublimation of carbonate of ammonia, when carbonate of lime and hydrochlorate of ammonia are heated together. As the order of affinity is often determined in mixed salts by volatility or insolubility, according to the canons of Berthollet, so it may be regulated and determined, in a similar sense, by diffusibility.

The application which I have particularly in view, is the possible decomposition of the sulphates of potash and soda, and of the chlorides of potassium and sodium, by means of lime, when the affinity of that base for an acid is aided by the high diffusibility of the hydrate of potash or of soda.

1. A solution was made of 1 part of sulphate of potash in 100 parts of lime-water, with which six phials were filled, and placed to diffuse in jars containing lime-water, instead of water simply, for the usual period of seven days. To obtain the salts diffused, the fluid of the jars was treated with an excess of bicarbonate of ammonia and evaporated twice to dryness. The filtered liquid contained only sulphate and carbonate of potash, without a trace of lime. The proportions of these salts found, indicated a diffusion-product from two phials of :

Hydrate of potash	.	.	.	1.08 grs.	23.69
Sulphate of potash	.	.	.	3.48 „	76.31
				4.56 „	100.00

The diffusion-product of the remaining four cells was similar :

Hydrate of potash	.	.	.	2.19 grs.	21.66
Sulphate of potash	.	.	.	7.94 „	78.34
				10.13 „	100.00

More than a fifth part of the diffused salt appears thus to be hydrate of potash, and a considerable decomposition of the sulphate of potash has therefore taken place.

2. Sulphate of soda dissolved in lime-water, was diffused into lime-water, in a precisely similar series of experiments.

The diffusion-product obtained in a set of four cells, appeared to consist of :

Hydrate of soda . . . .	0.90 grs.	11.45
Sulphate of soda . . . .	6.87 „	88.55
	<hr/>	<hr/>
	7.77 „	100.00

Of another set of four cells, the diffusion-product was represented by :

Hydrate of soda . . . .	0.93 grs.	13.22
Sulphate of soda . . . .	6.10 „	86.78
	<hr/>	<hr/>
	7.03 „	100.00

The hydrate of soda formed and diffused, is very sensible, amounting on an average to about 12 per cent of the whole diffused salt.

It may be remarked that, although sulphate of soda may be justly supposed to require a less powerful affinity to decompose it than sulphate of potash, still the latter salt appears to yield to the action of the lime to a greater extent than the former, in these experiments ; the weight of hydrate of potash diffused being fully double that of the hydrate of soda. The result in question may be confidently referred to the superior diffusibility of the hydrate of potash, and establishes, beyond doubt, the nature of the agency by which the decomposition, in both cases, is principally, if not wholly, effected.

The low diffusibility of the sulphate of lime (one fourth of that of hydrate of potash) retains a large proportion of that salt behind in the solution-phial, where, indeed, it was deposited in crystals. It is proper to remark, that a similar deposition of sulphate of lime took place in lime-water containing so much as 1 per cent of sulphate of potash or sulphate of soda, in the course of two or three days, in a close vessel, quite irrespective of diffusion. One of the solution-phials was found to contain so much as 2.04 grains of hydrate of potash, formed in consequence of this deposition of sulphate of lime, without any diffusion, in the course of seven days. The same decomposition of sulphate of potash, with deposition of sulphate of lime, was observed by Scheele, and afterwards referred, by Berthollet, to the insolubility of the latter salt, which enables the affinity of lime for sulphuric acid to prevail over that of potash for the same acid.



3. Similar solutions, of 1 per cent, of chlorides of potassium and sodium in lime-water, were diffused into lime-water.

Eight cells of chloride of potassium gave 25.51 grains of diffused salt, containing only 0.04 grain of hydrate of potash.

Eight cells of chloride of sodium gave 20.77 grains of diffused salt, containing no more than 0.08 grain of hydrate of soda.

The decomposition of the alkaline chlorides is so small as to be barely sensible, not exceeding, in the most favourable case, more than  $\frac{1}{250}$ th part of the salt diffused. Lime, therefore, appears incapable, although aided by diffusion, to decompose the chlorides of potassium and sodium to a sensible extent.

4. Solutions in lime-water were diffused of 0.25 and 0.5 per cent of the alkaline sulphates, not with the view of increasing the product of alkali, but for the purpose of observing the diffusion, where no deposition of sulphate of lime is possible, owing to the dilute condition of the solutions. The experiments, however, come to be more liable to derangement from currents produced by small changes of temperature, and other accidental causes of dispersion, where the solution in the phial differs so little in density from the water of the jar.

One set of four cells, containing the quarter per cent solution of sulphate of potassa in lime-water, gave 0.321 gr. of hydrate of potash. Another similar set gave 0.614 gr. of hydrate of potash. The hydrate of soda diffused from four cells of the quarter per cent solution of sulphate of soda was 0.260 gr. The diffusion was always into lime-water.

The half per cent solution of sulphate of potash in lime-water, gave 0.62 gr. hydrate of potash in two cells; or twice as much alkali as the quarter per cent solution. The diffusion-product was altogether 2.60 grs., so that 23.85 per cent of the salt diffused, consisted of hydrate of potash. No sulphate of lime crystallized, or was deposited in the phial or jar, in any of these experiments, so that the decomposition of the sulphate of potash by lime cannot be referred in any degree to the insolubility of sulphate of lime, but must be ascribed entirely to the high diffusibility of hydrate of potash.

5. Carbonate of lime dissolved in carbonic acid water, or a saturated solution of bicarbonate of lime, was now applied to form a 1 per cent solution of sulphates of potash and soda. These solutions were diffused from the phials into pure water, as the liquid atmosphere of the jars. Decomposition of the alkaline sulphate always took place, and without any visible deposit of sulphate of lime, but

to a less extent than in the preceding experiments with hydrate of lime. The proportion of potash salts diffused in two pairs of cells was 4.86 and 5.84 grs.; of which 0.26 and 0.30 gr. was carbonate of potash, or 5.35 and 6.2 per cent of carbonate of potash.

The proportion of soda-salts diffused in two pairs of cells was 3.40 and 3.78 grs., of which 0.26 and 0.29 gr. was carbonate of soda; or 7.65 and 7.67 per cent of carbonate of soda. The excess of carbonate of soda diffused over the carbonate of potash, in these experiments is probably accidental.

The experiments on the decomposition of an alkaline sulphate by means of carbonate of lime, aided by diffusion, are chiefly interesting, as they illustrate a decomposition which may occur among the salts of the soil, and with the formation of an alkaline carbonate, from a reaction between carbonate of lime and an alkaline sulphate, although the solutions may be too dilute to admit of any separation of sulphate of lime in the solid state.

But the decomposition of the chlorides of potassium and sodium is a more important problem than that of the sulphates of potash and soda. The direct diffusion of these chlorides with hydrate of lime appears to be inadequate to produce this effect, for no more than a trace of fixed alkali was obtained in the experiments already described. It was further observed, that a saturated solution of the chlorides of potassium and sodium in lime-water did not afford the smallest appreciable quantity of alkali by diffusion. Bicarbonate of lime had no greater effect upon the alkaline chlorides. But the conjoint action of lime-water and the sulphate of lime upon these chlorides gave better results.

6. Lime-water and solution of sulphate of lime, both saturated solutions, were mixed together in equal volumes, and the liquid was employed to dissolve 1 per cent of chloride of sodium. The phials charged with this solution were allowed to diffuse into pure water. After separating the hydrate of lime from the water of the jars, the latter exhibited only the faintest possible alkaline reaction due to soda. The proportion of alkali was too minute to be appreciated by the alkalimetric method, although a quantity so small as 0.01 gr. could be determined. To enable the hydrate and sulphate of lime to act upon the chloride of sodium, it was found necessary first to heat the solution before diffusion.

7. The solution of sulphate of lime, with an addition of 2 per cent of chloride of sodium, was kept at the boiling point for half an hour. No deposition of sulphate of lime occurred then, or after the liquid cooled. Two or three days afterwards, this solution was

mixed with an equal volume of lime-water, and diffused into pure water, for the short period of three and a half days. The liquid of the jars was evaporated to dryness, as usual, with an excess of pure carbonate of ammonia, to precipitate the salts of lime. The hydrate of soda diffused in three cells amounted to 0.234 gr., and the sulphuric acid to 0.209 gr. Allowing the sulphuric acid to have diffused as sulphate of soda, and putting out of consideration the undecomposed chloride of sodium which was also diffused, we have a diffusion-product of:

Hydrate of soda	.	.	0.234 gr.
Sulphate of soda	.	.	0.371 „
			<hr/>
			0.605 gr.

These quantities are necessarily small, from the form of the experiment, but could easily be increased by enlarging the diffusing surface, which is at present limited to the area of the aperture of the solution phial. They are amply sufficient, however, to establish the fact that the united affinities of hydrate and sulphate of lime are sufficient to decompose chloride of sodium, when aided by diffusion of the hydrate of soda formed. Of chloride of potassium, we have reason to believe that the decomposition would be more considerable in similar circumstances.

Two phials of the same liquid as in the last experiment were diffused into water for the longer period of seven days and eighteen hours. The whole lime found afterwards in the water-jar, and precipitated by the addition of carbonate of ammonia, was represented by 1.01 grain of carbonate of lime. The soluble salts filtered from the last amounted to 6.14 grains, and contained carbonate of soda equivalent to 0.646 gr. of hydrate of soda, and sulphuric acid equivalent to 0.373 gr. of sulphate of soda. It is difficult to decide in what form the lime reached the water-jar, but this earth was probably diffused out of the solution-phial, partly as hydrate of lime, partly as sulphate of lime, but principally as chloride of calcium. The last two salts would destroy a portion of free alkali in the evaporation, but the hydrate of soda obtained, even after this deduction, amounted to 10.52 per cent of the whole salts diffused. With a smaller quantity of chloride of sodium than 2 per cent in the original mixture, the alkali, although not increased in absolute quantity, might no doubt come to form a considerably larger proportion of the diffusion-product.

The experiments also throw a curious light upon the condition of

mixed salts. It follows, from the absence of hydrate of soda in the diffusion product of the first experiments, that cold solutions of sulphate of lime and chloride of sodium may be mixed without decomposition, or without any sensible formation of sulphate of soda. But on heating, this change is induced, and it is permanent; sulphate of soda is formed, and continues to exist in the cold solution: for it is the decomposition of that salt alone, by hydrate of lime, which appears to afford the diffused hydrate of soda. More than one condition of equilibrium is therefore possible for mixed solutions of sulphate of lime and chloride of sodium. It would be interesting to submit such a mixture to a diffusion experiment, after being kept for different periods. The effects of time and temperature are so often convertible, that we might anticipate a gradual formation of sulphate of soda. If such be the case, we have an agency in the soil, by which the alkaline carbonates required by plants may be formed from the chlorides of potassium and sodium, as well as from the sulphates of potash and soda; for the sulphate of lime generally present will convert those chlorides into sulphates.

The mode in which the soil of the earth is moistened by rain is peculiarly favourable to separations by diffusion. The soluble salts of the soil may be supposed to be carried down together, to a certain depth, by the first portion of rain which falls, while they find afterwards an atmosphere of nearly pure water, in the moisture which falls last and occupies the surface stratum of the soil. Diffusion of the salts upwards into this water, with its separations and decompositions, must necessarily ensue. The salts of potash and ammonia, which are most required for vegetation, possess the highest diffusibility, and will rise first. The pre-eminent diffusibility of the alkaline hydrates may also be called into action in the soil by hydrate of lime, particularly as quick-lime is applied for a top-dressing to grass lands.

**NOTICES**  
OF  
**PAPERS CONTAINED IN THE FOREIGN JOURNALS.**  
BY HENRY WATTS, B.A., F.C.S.

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**On the presence of Lead, Copper, and Silver in Sea-Water, and on the existence of the latter in Plants and Animals.**

**By MM. Malaguti, Durocher, and Sarzeaud.\***

The existence of silver in sea-water was suspected by the authors from the following considerations; it is extensively diffused in the mineral kingdom: it is easily converted into chloride by the action of salt-water; its chloride is soluble in other chlorides, especially in chloride of sodium; and its sulphide is readily acted upon by sea-water, and converted into chloride. Further, as silver frequently accompanies galena, and that mineral always contains small quantities more or less appreciable, of iron, zinc, and copper, it seemed probable that these metals might also be found in sea-water. The authors' researches were limited to the detection of silver, lead, and copper—the presence of iron being already known, and the detection of zinc in very minute quantities being almost impossible, for want of a test of sufficient delicacy.

As the quantity of the above metals in sea-water is extremely small, the utmost care was necessary to ensure that they were not introduced by the reagents employed in the analyses. The silver, after precipitation by sulphuretted hydrogen or otherwise, was alloyed with lead, by fusing the precipitate with litharge and reducing agents, as free from silver as they could be obtained, and the metallic button thus produced was cupelled to separate the silver—a comparative experiment being made in every instance with the same materials, but without the silver-precipitate, in order that any error arising from the presence of traces of silver in the reagents, might be detected and allowed for. The water used for solution, washing, &c., was spring-water, containing but a very small quantity of solid matter, and ascertained by careful examination to be quite free from silver. This was considered preferable to distilled water, inasmuch

\* Ann. Ch. Phys. [3] XXVIII, 129.

as the latter might have taken up traces of silver, by being kept in vessels of tinned copper, or by contact with the solder at the joints of the tin tubes in the distilling apparatus, since copper, tin, and lead, frequently contain minute quantities of silver.

*Silver in sea-salt.*—400 grms. of sea-salt fused with 25 grms. litharge, and 1 gm. lamp-black, yielded a button of lead which left a very small button of silver on the cupel, whereas, the same quantity of lead extracted from the same litharge left nothing upon the cupel. This preliminary trial was checked by precipitation with sulphuretted hydrogen.—3 kilogrammes of crude-salt (obtained from salt-marshes, and not subjected to any purifying process whatever) were dissolved in 24 litres of the spring-water above-mentioned, and the solution saturated by sulphuretted hydrogen purified by two washings. The liquid became opalescent, but after standing for two months, it regained its transparency and deposited a greyish-white precipitate. This deposit was cupelled with 3 grms. of pure lead, and a button of silver obtained, but not much larger than that produced by the former method from a much smaller quantity of salt. From this, it would appear that sulphuretted hydrogen does not precipitate the whole of the silver contained in a solution of sea-salt; and in fact, if such a solution be precipitated as completely as possible by sulphuretted hydrogen, and afterwards evaporated to dryness, the residue, if treated with lead and cupelled, as above, will yield a button of silver.

*Estimation of silver in sea-water.*—A considerable quantity of sea-water was taken from off the coast of St. Malo, a few leagues from land, and preserved during the course of the experiments in a wooden cistern, from which it was taken out, as occasion required, in glass vessels. The presence of silver in this water was first demonstrated by the sulphuretted hydrogen process above described; but in order to obtain a more exact estimation of the quantity, 50 litres of the water were evaporated to dryness, and the crude-salt thence obtained, weighing 1300 grammes, was divided into 13 equal portions, and each portion fused with 30 grms. of pure litharge and 1.13 grms. of lamp-black. This mixture, which was made very intimate by long trituration in a porcelain mortar, was gradually heated to dull redness in a crucible, and maintained at that temperature for fifteen or twenty minutes; the heat was then gradually raised till the mixture fused, and afterwards increased to whiteness: as soon as that temperature was attained, the crucible was withdrawn from the fire. Thirteen operations of this kind yielded 124 grms. of lead, and the silver contained in this was found by cupellation (deducting that which was yielded by the lead alone, in a test experiment) to amount to 0.0005 gm. Now, as this demi-milligramme of silver was extracted from 50 litres of sea-water, it follows that 100 litres—or for simplicity, say 100 kilogrammes of sea-water—contain 1 milligramme; hence, the proportion of salt in sea-water is, approximately, 1 part in



100,000,000, so that a cubic myriametre of sea-water contains 1000 kilogrammes, or a cubic mile (English) contains about  $2\frac{3}{4}$  lb. avoirdupois. This estimation must be regarded as a minimum; for all the preceding operations are attended with slight loss.

*Silver in Fuci.*—The well-known faculty which plants possess, of condensing within their substance certain of the principles which form the medium in which they grow, induced the authors to search for silver in sea-weed, with the full expectation that these plants would be found to contain it in larger proportion than the sea-water itself. The species examined were *Fucus canaliculatus*, *F. vesiculosus*, *F. serratus*, *F. ceramoides*, *F. nodosus*; *Ulva compressa*. These plants were incinerated by burning them on an iron grating supported on four feet resting on plates of porcelain, the whole apparatus having never been used for any other operation. The ashes of all these species yielded buttons of silver by cupellation. 100 grms. of the ashes of *Fucus serratus* yielded 0.001 grm. silver; the same proportion was found in the ashes of *Fucus ceramoides*; the other species yielded buttons too small to be weighed. The proportion of silver contained in the ashes of *Fucus serratus* and *ceramoides* is  $\frac{1}{10000}$ . From this it is calculated that the fuci are about 26 times as rich in silver as the water itself.

By similar methods, the authors have demonstrated the existence of silver in various chemical products, in the preparation of which sea-salt is employed, *e. g.*, in carbonate of soda and hydrochloric acid. The quantity of silver in carbonate of soda was found to be greater than that in the sea-salt itself. The excess arises from the use of sulphuric acid in the preparation, that acid always containing lead, and therefore also silver.

The wood of various trees, *e. g.*, the oak, birch, beech, hornbeam, aspen, apple, and ash, grown at a considerable distance from the sea, and on land which had never been manured with salt or sea-weed, likewise yielded ashes in which silver was detected. The presence of silver in these plants appears therefore to be connected with the general distribution of silver in the mineral kingdom—a fact previously established by the experiments of two of the authors of this memoir. The blood of an ox was likewise found to contain silver, derived of course from the vegetable substances on which the animal had fed. These experiments are sufficient to show that the occurrence of silver in organic substances is by no means uncommon, although they cannot safely be regarded as a proof of the constancy of its occurrence.

With regard to the question whether the silver in the waters of the ocean has been carried thither by rivers in recent times, and derived from the waste of that which is used by man, or whether its existence therein is of more ancient date—the authors observe, in the first



place, that, supposing the proportion of silver in all parts of the ocean to be the same as that which was found in the particular portion examined, the total quantity contained in the ocean would amount to about 2,000,000 tons, a quantity which is probably greater than that which has even been extracted from the earth by artificial means. The question, however, is more completely decided by the examination of marine deposits anterior to the existence of man upon the earth. For this purpose, the authors searched for silver in *rock-salt* occurring in sedimentary strata and deposited from ancient salt lakes or marine basins, and likewise in *coal*. In the *rock-salt*, the presence of silver was demonstrated beyond all doubt; the ashes of the *coal* likewise yielded a button of silver, but the authors consider that the result of the experiment is rendered somewhat doubtful, partly by the possible occurrence of iron pyrites in the *coal* (though the most careful examination failed in detecting any), and partly in consequence of the large quantity of the reagents which it was found necessary to use. The occurrence of silver in the *rock-salt* is, however, quite sufficient to show that the presence of that metal in sea-water is of ancient date.

*Lead and copper in Fuci.*—Ten kilogrammes of a mixture of several species of fucus, chiefly *F. serratus*, *nodosus*, and *ceramoides*, gathered on the coast of St. Malo, were incinerated, and yielded 1.7 kilogrammes of ashes. These ashes were washed with a large quantity of water to free them from soluble salts, especially sulphate of lime, which they contain in large quantity. The residue was then digested in hot nitric acid, not in excess, the liquid left to stand for several days, and then mixed with a large quantity of spring-water, all these operations being conducted in porcelain basins. After filtration, the liquid was introduced into a glass vessel, and saturated with sulphuretted hydrogen previously washed; a very light, flocculent, greyish precipitate was soon formed, consisting chiefly of sulphate of lime. The whole was then left at rest for several weeks; the liquid filtered; and when the filter was dry, the sulphate of lime was easily removed by a feather. There was then left on the filter a very thin film of a brownish colour. As this could not be detached, the filter was burnt over a porcelain capsule; the ashes dissolved in nitric acid; the liquid diluted with water, and filtered, and then strongly acidulated with sulphuric acid. It immediately became turbid, and after a few hours, a white heavy precipitate settled down, which, when washed and dried, weighed 0.047 grm. From this precipitate, a button of lead was easily obtained by the blow-pipe. Now, as the quantity of ashes operated upon was 1700 grms., and as 32 parts of lead correspond to 47 of sulphate, it follows that the

ashes contain at least  $\frac{12}{1,000,000}$  of their weight of lead. The nitric acid, the sulphuric acid, the filter-paper, and the glass used in the

experiments were examined for lead with the utmost care, and were found to be quite free from it. The experiments were repeated three times, and always with the same result.

The presence of *copper* in the sea-weed was demonstrated by two distinct processes.—1. The acid liquid separated by filtration from the sulphate of lead in the operation above described, was supersaturated with ammonia and then filtered: the clear solution had a blue tint. It was again saturated with acid, and a bright iron wire immersed in it; the wire soon became coated with metallic copper.—2. 1275 grms. of sea-weed (undried) were introduced into a large glass vessel previously washed out with aqua-regia, and a sufficient quantity of spring-water added to immerse them completely. The liquid was then saturated with chlorine gas previously well washed, the vessel closed, and the whole left at rest for twenty-four hours. This operation was repeated every day, till the fuci were completely bleached and no further action took place. After this, the liquid was concentrated by evaporation in a porcelain basin, then saturated with ammonia, filtered, and neutralized with pale acetic acid. The neutral solution treated with a few drops of ferrocyanide of potassium, gave the characteristic red-brown colour indicative of the presence of copper. These experiments sufficiently establish the presence of lead and copper in fuci, and therefore also in sea-water. The fuci were chosen in preference to other marine plants, because, having no real roots, they do not insert themselves into the rocks, but merely rest upon them, and must therefore derive all their mineral constituents from the water.

In conclusion, the authors observe, that the presence of silver, copper, and lead, in sea-water, though it may appear singular on first consideration, will be easily understood, if it be remembered that the sulphides of lead and copper are very widely diffused in nature, as likewise is the sulphide of silver, either alone or associated with other metals. Now salt-water attacks all these sulphides, and converts them into chlorides, which it dissolves. The waters which circulate through the upper parts of the earth's crust, and which almost always contain chlorides and other salts of the alkalis, react in the same manner on these natural sulphides, dissolving out small quantities of metal, which they carry away and transfer to the tissues of plants; lastly, the same waters contribute, together with the solid food, to introduce these metals into the bodies of animals.

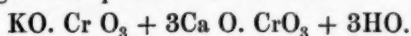
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**On a Chromate of Copper and Potash.**

By A. Knop.\*

When bichromate of potash is poured upon recently precipitated hydrated oxide of copper, a light brown, crystalline compound is formed, composed of small hexagonal tables. This salt is insoluble in water. Carbonate of ammonia and caustic ammonia dissolve it, producing a deep green solution. This solution, if saturated while hot and then left to cool, deposits brilliant green prisms, having a golden lustre by reflected light; these crystals appear to be the chromate of copper and ammonia described by Malaguti.

The same chromate of copper and potash is obtained by mixing a solution of sulphate of copper with excess of bichromate of potash, and gradually adding caustic potash. It contains:

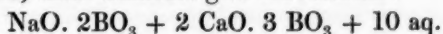
**On a native Borate.**

By G. L. Ulex.†

Beneath the nitre beds of Southern Peru, there are found white, tuberculous masses, which, in that country, are called *Tiza*. In size they vary from a hazel-nut to a middling sized potato, and have exactly the external appearance of the *Aluminite* described by Halle; but the fractured surfaces show that the mass is composed of soft, white, silky fibres interlacing each other; they absorb water rapidly, and have a slightly saline taste. Embedded in the tuberculous masses, are sometimes found sharp-edged fragments of *Andesite*, and of quartzose and argillaceous minerals, and, *invariably*, large rhombic prisms of *Brogniartın*. The density of the crystalline fibres is 1.8; their form appears to be that of a hexagonal prism, or perhaps a rhombic prism with the acute lateral edges truncated. Their composition is as follows:

Boracic acid . . . . .	49.5	49.5
Lime . . . . .	15.7	15.9
Soda . . . . .	8.8	8.8
Water . . . . .	26.0	25.8
	<hr/>	<hr/>
	100.0	100.0

Assuming that the relation of the boracic acid to the soda is the same as in borax, these numbers give the formula:



The author is of opinion that this mineral is identical with the *Hydro-borocalcite* described by Hayes.

The brogniartın, with which this borate is mixed, consists of sulphate of soda and lime:



\* Ann. Ch. Pharm. LXX, 52.

† Ibid. LXX, 49.

### On the Preparation of Hydrobromic and Hydriodic Acids.

By Ch. Mene.\*

M. Mene recommends, for the preparation of these gases, the use of crystallized hypophosphite of lime, resulting from the preparation of phosphuretted hydrogen, by means of phosphuret of lime, or else sulphate of soda in the state in which it is found in commerce. The proportions are as follows :

Water . . . . .	1 pt.	or,	Water . . . . .	1 pt.
Iodine or bromine . . . . .	5 „ „		Iodine or bromine . . . . .	3 „
Hypophosphite (cryst) . . . . .	4 „ „		Sulphite (cryst) . . . . .	6 „

The hypophosphite of lime is introduced into a flask or a retort, together with a small quantity of water, and liquid bromine poured in by means of a funnel. The reaction takes place in the cold; but it is indispensable to put into the neck of the retort or flask, a few pieces of cotton or asbestos, in order to retain the vapour of bromine, which would otherwise be volatilized by the heat evolved. The operation is the same with iodine, excepting that it is necessary to apply a gentle heat.

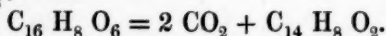
The use of crystallized sulphite of soda is more economical, because it is a commercial product. The crystals are simply moistened with water, then iodine or bromine added, and a gentle heat applied.

These two processes are not attended with the dangerous explosions to which the old method is liable.

### On Anisol and Phenetol.

By A. Cahours.†

In a former memoir,‡ M. Cahours has shown that, when anisic acid, or its analogue, the salicylate of methyl, is distilled in contact with an excess of baryta, the baryta is transformed into carbonate, and a limpid, colourless liquid distils over, having the composition,  $C_{14}H_8O_2$  :



To this liquid, Cahours gives the name of *Anisol*.

By the action of fuming nitric acid upon anisol, three distinct products are formed, according to the proportions used, and the rapidity of the action. If the acid is added in small portions at a time, and the containing vessel is surrounded with pounded ice, to prevent rise of temperature, a liquid product is formed, which differs from anisol merely by the substitution of 1 eq. hyponitric acid for 1 eq. hydrogen. This compound is called *Mononitranisol*,  $C_{14}H_7NO_6$ . It is a limpid amber-coloured liquid, heavier than water, boiling between  $262^0$  and  $264^0$  C., and having an aromatic odour, somewhat like that of bitter almonds. Caustic potash, in

\* Compt. Rend. XXVIII, 478.

† Ann. Ch. Phys. [3] 27, 439.

‡ Ann. Ch. Phys. [3] 10, 327.

solution, has no action upon it; strong sulphuric dissolves it with the aid of a gentle heat; water added to the liquid separates the anisol unaltered. When heated with fuming nitric acid, it is converted into binitranisol, and subsequently into trinitranisol.

When anisol is treated with fuming nitric acid in excess, the liquid boiled for a few minutes, and then water added, a yellow liquid separates, which quickly aggregates into an amber-coloured mass, easily soluble in boiling alcohol, and separating from the solution, on cooling, in the form of long, yellowish needles. This compound is *Binitranisol*,  $C_{14}H_6N_2O_{10}$ , formed from anisol by the substitution of 2 eq. hyponitric acid for 2 eq. hydrogen.—By treating anisol with a mixture of equal parts of sulphuric acid and fuming nitric acid, a third compound is formed, in which 3 eq. of hydrogen are replaced by hyponitric acid: this is *Trinitranisol*. When first formed, it is a heavy, oily liquid, but soon aggregates into a hard mass, of a clear, yellow colour: it is perfectly insoluble in water.

*Action of Hydrosulphate of Ammonia on the preceding Compounds.*

1. *Anisidine*.— $C_{14}H_9NO_2$ .—When an alcoholic solution of hydrosulphate of ammonia is brought in contact with mononitranisol, an energetic reaction takes place, sulphur being deposited, and a basic substance formed by the substitution of 1 eq.  $NH_2$  for 1 eq.  $NO_4$ . This base is *Anisidine*. To obtain it in a state of purity, the alcoholic solution is evaporated at a gentle heat, till it is reduced to a third or a fourth of its original bulk, then mixed with a slight excess of hydrochloric acid, and filtered, after the addition of a small quantity of water, in order to separate sulphur. The filtered liquid, evaporated at a gentle heat, deposits crystals of the hydrochlorate of the new base; and these crystals, when distilled with a concentrated solution of potash, yield the anisidine in the form of an oily liquid, which solidifies in crystals, on cooling. *Hydrochlorate of anisidine* crystallizes in fine, colourless needles. When a hot, concentrated solution of this salt is mixed with a concentrated solution of bichloride of platinum, yellow needles of a double salt are deposited on cooling. Anisidine likewise forms crystalline compounds with oxalic, nitric, and sulphuric acid.

2. *Nitranisidine*.— $C_{14}H_8N_2O_6$ .—Formed by mixing an alcoholic solution of binitranisol with hydrosulphate of ammonia. The solution is then evaporated to a third of its bulk, mixed with a slight excess of hydrochloric acid, filtered, and the filtered solution treated with ammonia. A red, crystalline precipitate is then thrown down, which is washed with distilled water, and dissolved in boiling alcohol. The solution, left to cool slowly, deposits the base in long needles, having the colour of garnet and considerable lustre. It is insoluble in cold water, but dissolves with tolerable facility in boiling water, and the solution solidifies in a mass on cooling. Boiling alcohol dissolves it with facility. Ether likewise dissolves it readily, especially when



warmed. The solution, if left to spontaneous evaporation, deposits the base in long, orange-coloured needles. With nitric, sulphuric, hydrochloric, and hydrobromic acid, nitranisidine forms salts which crystallize very distinctly. The sulphate, when pure, is perfectly colourless. The hydrochlorate forms, with bichloride of platinum, a double salt which crystallizes in orange-brown needles.

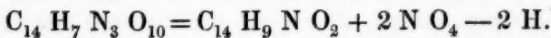
**Nitro-benzanisidide.**— $C_{28}H_{12}N_2O_8$ . When crystals of nitranisidine are dropt into chloride of benzoyl, no action takes place in the cold; but on gradually raising the temperature, a brisk action soon commences; hydrochloric acid is given off; and a compound is formed analogous to benzamide and benzanilide. The solid mass thus produced is then treated successively with water, hydrochloric acid, and an alkaline solution, to free it from benzoic acid and nitranisidine. It is then washed several times with distilled water, and dissolved in a quantity of alcohol just sufficient to take it up at a boiling heat: it then separates in a state of purity on cooling. This substance crystallizes in small needles of a blonde colour. It is insoluble in water both hot and cold, and scarcely soluble in alcohol at ordinary temperatures. Fuses when gently heated, and volatilizes at a higher temperature. Dissolves in strong sulphuric acid when gently heated, imparting a deep red-brown colour to the liquid.

**Nitro-cinnanisidide.**— $C_{32}H_{14}N_2O_8$ .—Obtained in the same manner as the preceding compound, by the use of chloride of cinnyl instead of chloride of benzoyl. Dissolves sparingly in cold alcohol, and with tolerable facility in boiling alcohol, from which, on cooling, it separates in small yellowish needles.

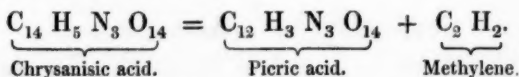
Similar products are likewise obtained by the action of *chloride of cumyl* and *chloride of anisyl* on nitranisidine.

3. **Binitranisidine.**— $C_{14}H_7N_3O_{10}$ .—Formed by digesting trinitranisol at a gentle heat with an alcoholic solution of hydrosulphate of ammonia. Separated by converting into a hydrochlorate, and treating the solution with excess of ammonia. It is then gradually deposited in the form of red flakes, which, after being repeatedly washed with distilled water, and then dried either *in vacuo*, or over the water-bath, are converted into a powder which exhibits a bright red or a violet-red colour, according to the strength of the solution from which it was precipitated; it is quite destitute of crystalline character. Cold water dissolves but a mere trace of this compound; boiling water dissolves it in small quantities. Cold alcohol dissolves but little of it; boiling alcohol takes it up pretty readily, and if slowly cooled, deposits it in the form of blackish violet-coloured needles, resembling crystals of cinnabar. Slightly soluble in warm ether, from which it separates in needles of a very deep violet colour. Fuses at a moderate heat, and solidifies, on cooling, in a radiated, crystalline mass, having a blackish-violet colour, and resembling cinnabar. With hydrochloric, nitric, and sulphuric acid, binitranisidine forms salts which are soluble and crystallizable if the acid be

added in excess; but water decomposes them, setting the base at liberty. Fuming nitric acid attacks it strongly at a boiling heat, producing a substance of a brownish-yellow colour like resin, which dissolves in potash and then assumes a very deep brown colour. Binitranisidine may be considered as anisidine with 2 equivalents of hyponitric acid substituted for 2 equivalents of hydrogen:



*Chrysanisic acid.*— $C_{14} H_5 N_3 O_{14}$ .—When anisic or nitranisic acid is treated with fuming nitric acid, binitranisol and trinitranisol are formed, and likewise an acid product which is soluble in hot alcohol, and crystallizes, on cooling, in the form of rhomboidal scales of a magnificent golden-yellow colour. This compound is *chrysanisic acid*; it is isomeric with trinitranisol, and therefore a homologue of picric acid (trinitrophenol). It may in fact be regarded as picric acid *plus* 1 eq. methylene ( $C^2 H^2$ ).



This acid is not sensibly soluble in cold water; boiling water dissolves it in small quantities, and deposits it in crystals on cooling. Alcohol, at ordinary temperatures dissolves but a mere trace of it; boiling alcohol dissolves it abundantly, so that a saturated solution solidifies in a mass on cooling. Ether dissolves it, especially when warm, and, on evaporation, deposits it in very brilliant yellow laminæ. Fuses when carefully heated, and on cooling solidifies in a crystalline mass: when more strongly heated, it gives off a yellow vapour, which condenses on the sides of the retort in small, very brilliant scales. When boiled with strong nitric acid, it is converted into picric acid. By distillation with chloride of lime, it yields a large quantity of chloropicrine. When mixed with a quantity of potash just sufficient to saturate it, it forms a very soluble salt; an excess of potash decomposes it, converting it into a brown substance.

*Chrysanisate of ammonia*,  $C_{14} H_5 N_4 O_{14}$ , crystallizes in small needles. Its solution precipitates a great number of metallic salts—forming, with salts of protoxide of copper, a yellowish-green gelatinous precipitate; with salts of sesquioxide of iron, light yellow; with zinc-salts a precipitate similar to the last, but lighter; with protochloride of mercury, no immediate precipitate, if the solutions are dilute; yellowish-red flakes, if they are concentrated; with nitrate of lead, a copious flocculent precipitate of a fine chrome-yellow colour; with nitrate of silver, a fine yellow, flocculent precipitate; and with nitrate of cobalt, a gelatinous precipitate of a yellow colour slightly tinged with green.—*Chrysanisate of silver*,  $C_{14} (H_4 Ag) N_3 O_{14}$ , is precipitated in fine yellow flakes, on mixing solutions of nitrate of silver and chrysanisate of ammonia.



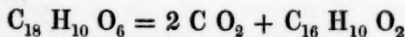
*Chrysanisic ether*,  $C_{18} H_9 N_3 O_{14}$  is obtained by passing dry hydrochloric acid gas into a solution of chrysanisic acid in strong alcohol till it is no longer absorbed; then boiling the liquid gently for a short time, and adding water. A voluminous precipitate is then produced, which must be thrown on a filter, and washed with water containing ammonia, to remove any chrysanisic acid that may remain unaltered. It is afterwards washed with pure water, and then dissolved in boiling alcohol, which, on cooling, deposits it in transparent scales of a very rich golden-yellow colour. Dissolves in warm ether; fuses at about  $100^{\circ}$ .

*Sulphanisolide*.— $C_{14} H_7 S O_4$ .—When vapour of anhydrous sulphuric acid is passed into anisol artificially cooled, the vapour is gradually absorbed and the liquid thickens. If water be then added, three products are formed, viz.: anisol unaltered, *sulphanisolic acid*, and *sulphanisolide*, which is a solid substance analogous to *sulphabenzide*; it forms delicate needles, having a silvery lustre and easily soluble in alcohol and ether.

#### DERIVATIVES OF SALICYLIC ETHER.

When chlorine gas is passed in excess through salicylic ether (salicylate of ethyl) heated over a water-bath, a solid substance is formed which is soluble in hot alcohol, and crystallizes, on cooling, in beautiful colourless tables. This compound is *bichloruretted salicylic ether*, formed from salicylic ether ( $C_{18} H_{10} O_6$ ) by the substitution of 2 eq. chlorine for 2 eq. hydrogen: its composition is therefore  $C_{18} H_8 Cl_2 O_6$ . The corresponding bromine compound, which forms magnificent crystals, is obtained in a similar manner. When salicylic ether is acted upon by a mixture of sulphuric and fuming nitric acid, a product is obtained which dissolves in boiling alcohol, and crystallizes, on cooling, in beautiful white scales, with a faint tinge of yellow. This compound is *Binitro-salicylic ether*, formed by the substitution of 2 eq.  $N O_4$  for 2 eq. hydrogen: hence its composition is  $C_{18} H_8 (N O_4)_2 O_6 = C_{18} H_8 N_2 O_{14}$ .

*Phenetol*.— $C_{16} H_{10} O_2$ .—Salicylic ether forms definite compounds with caustic alkalies. On distilling the baryta compound, the salicylic ether is resolved into 2 eq. carbonic acid and 1 eq. phenetol, which distils over:



Phenetol is a colourless, very mobile liquid, lighter than water; and having an agreeable, aromatic odour; it is insoluble in water, but dissolves readily in alcohol and ether. Solution of caustic potash has no effect upon it. Sulphuric acid converts it into a copulated acid. Chlorine and bromine convert it into crystallizable products.

*Binitrophenetol*.— $C_{16} H_8 N_2 O_{10}$ .—Formed by the action of fuming nitric acid at a boiling heat on phenetol. Crystallizes in yellow needles, much like those of binitranisol, of which this compound is the homologue.

**Nitrophenitidine.**— $C_{16} H_{10} N_2 O_6$ .—Formed by passing sulphuretted hydrogen and ammoniacal gas through an alcoholic solution of binitrophenetol. Crystallizes in brown needles. This compound is a base, analogous to nitranisine, and forms crystallizable compounds with sulphuric, nitric, and hydrochloric acid. The other homologues of the anisol series, M. Cahours has not yet formed, but there can be no doubt of their existence.

The following table contains all the derivatives of salicylate of methyl and salicylate of ethyl described by M. Cahours in this and in former memoirs, the bodies of the second group differing from the first only by the addition of  $C^2 H^2$ .

FIRST GROUP.				SECOND GROUP.			
$C_{16}$	$H_8$	$O_6$	Salicylate of methyl.	$C_{16}$	$H_8$	$O_6 \cdot C_2 H_2$	Salicylic ether.
$C_{16}$	$\left\{ \begin{smallmatrix} H_7 \\ Cl \end{smallmatrix} \right\}$	$O_6$	Monochloruretted salicylate of methyl.	$C_{16}$	$\left\{ \begin{smallmatrix} H_7 \\ Cl \end{smallmatrix} \right\}$	$O_6 \cdot C_2 H_2$	Monochlor. salicylic ether.
$C_{16}$	$\left\{ \begin{smallmatrix} H_6 \\ Cl_2 \end{smallmatrix} \right\}$	$O$	Bichloruretted salicylate of methyl.	$C_{16}$	$\left\{ \begin{smallmatrix} H_6 \\ Cl_2 \end{smallmatrix} \right\}$	$O_6 \cdot C_2 H_2$	Bichlor. salicylic ether.
$C_{16}$	$\left\{ \begin{smallmatrix} H_7 \\ Br \end{smallmatrix} \right\}$	$O$	Monobromuretted salicylate of methyl.	$C_{16}$	$\left\{ \begin{smallmatrix} H_7 \\ Br \end{smallmatrix} \right\}$	$O_6 \cdot C_2 H_2$	Monobrom. salicylic ether.
$C_{16}$	$\left\{ \begin{smallmatrix} H_6 \\ Br_2 \end{smallmatrix} \right\}$	$O_6$	Bibromuretted salicylate of methyl.	$C_{16}$	$\left\{ \begin{smallmatrix} H \\ Br_2 \end{smallmatrix} \right\}$	$O_6 \cdot C_2 H_2$	Bibromuretted salicyl. ether.
$C_{16}$	$\left\{ \begin{smallmatrix} H_7 \\ NO_4 \end{smallmatrix} \right\}$	$O$	Mononitro-salicylate of methyl.	$C_{16}$	$\left\{ \begin{smallmatrix} H_6 \\ NO_4 \end{smallmatrix} \right\}$	$O_6 \cdot C_2 H_2$	Mononitro-salicylic ether.
$C_{16}$	$\left\{ \begin{smallmatrix} H_6 \\ (NO_4)_2 \end{smallmatrix} \right\}$	$O_6$	Binitro-salicylate of methyl.	$C_{16}$	$\left\{ \begin{smallmatrix} H_5 \\ (NO_4)_2 \end{smallmatrix} \right\}$	$O_6 \cdot C_2 H_2$	Binitro-salicyl. ether.
$C_{16}$	$H_8$	$O_6$	$-2 C O_2 = C_{14} H_8 O_2$ Anisol.	$C_{16}$	$H_8$	$O_6 \cdot C_2 H_2$	$-2 CO_2 =$ $C_{14} H_8 O_2 \cdot C_2 H_2$ Phenetol.
$C_{14}$	$\left\{ \begin{smallmatrix} H_7 \\ NO_4 \end{smallmatrix} \right\}$	$O_2$	Nitranisol.	$C_{14}$	$\left\{ \begin{smallmatrix} H_7 \\ NO_4 \end{smallmatrix} \right\}$	$O_3 \cdot C_2 H_2$	Nitrophenetol.
$C_{14}$	$\left\{ \begin{smallmatrix} H_6 \\ (NO_4)_2 \end{smallmatrix} \right\}$	$O_2$	Binitranisol.	$C_{14}$	$\left\{ \begin{smallmatrix} H_6 \\ (NO_4)_2 \end{smallmatrix} \right\}$	$O_2 \cdot C_2 H_2$	Binitrophenetol.
$C_{14}$	$\left\{ \begin{smallmatrix} H_5 \\ (NO_4)_3 \end{smallmatrix} \right\}$	$O_2$	Trinitranisol.	$C_{14}$	$\left\{ \begin{smallmatrix} H_5 \\ (NO_4)_3 \end{smallmatrix} \right\}$	$O_2 \cdot C_2 H_2$	Trinitrophenetol.
$C_{14}$	$H_9$	$N O_2$	Anisidine.	$C_{14}$	$H_9$	$N O_2 \cdot C_2 H_2$	Phenetidine.
$C_{14}$	$\left\{ \begin{smallmatrix} H_8 \\ NO_4 \end{smallmatrix} \right\}$	$NO_2$	Nitranisidine.	$C_{14}$	$\left\{ \begin{smallmatrix} H_8 \\ NO_4 \end{smallmatrix} \right\}$	$NO_2 \cdot C_2 H_2$	Nitrophenitidine.
$C_{14}$	$\left\{ \begin{smallmatrix} H_7 \\ (NO_4)_2 \end{smallmatrix} \right\}$	$NO_2$	Binitranisidine.	$C_{14}$	$\left\{ \begin{smallmatrix} H_7 \\ (NO_4)_2 \end{smallmatrix} \right\}$	$NO_2 \cdot C_2 H_2$	Binitrophenetidine.

**On the Characteristic Properties of the two Acids which compose Racemic Acid.**

**By M. L. Pasteur.\***

Pasteur has shown that racemic or paratartaric acid is a compound of two acids, one of which turns the plane of polarization of luminous rays to the right, the other to the left, hence called *Dextro-racemic acid* and *Levo-racemic acid*. These two acids enter into racemic acid in equal quantities; and their crystalline forms, which are identical in all their individual parts, are *symme-*

\* Ann. Ch. Phys. [3] XXVIII, 56.

*trical*\* *polyhedrons*, incapable of coinciding by superposition. The corresponding salts of these acids likewise exhibit the most striking analogies in their physical and chemical properties; the only difference between them consisting in the opposite directions in which they turn the plane of polarization of luminous rays, and in the *symmetry* of their crystalline forms. Dextroracemic acid is identical with tartaric acid.

*Racemate of Soda and Ammonia*.—This is the salt by which the separation of the two acids is effected. When equal weights of racemic acid are saturated, the one with soda and the other with ammonia, and the neutral solutions mixed, the liquid, by cooling or by spontaneous evaporation, deposits a double salt in remarkably fine crystals, which, if the liquid be left to itself for three or four days, often attain the length of several centimetres. These crystals are rectangular prisms, having their lateral edges replaced by planes; and the intersection of *two* only of these planes with the terminal faces of the prism are replaced by facets; hence the crystals are hemihedral. Further, on minutely examining these crystals, one by one, it is found that they may be divided into two groups, the crystals in the one having the hemihedral facets symmetrically situated to those in the other.

The crystals of one of these groups turn the plane of polarization to the right; those of the other, to the left. In other respects, the crystals of the two groups are absolutely identical. It is impossible to obtain a complete separation of the two kinds of crystals by merely picking them out; but after separating them in this way as well as possible, and drying them on bibulous paper to remove the adhering mother-liquid, complete purification may be effected by dissolving the crystals of the dextroracemate and levoracemate in separate portions of water, and crystallizing again.—That these crystals are really of different kinds, and that neither of them, taken alone, contains racemic acid, may be shown by dissolving one of them in water, and treating the solution with a lime-salt. If the solution be somewhat dilute, no precipitate will be formed at first; but after a while, brilliant, isolated crystals will be formed, consisting of right rhombic prisms, passing into the octohedral form at the angles of the base; in short, the lime-salt is precipitated with all the characters of tartrate of lime. The solutions of both kinds of crystals behave in the same manner. But, if instead of taking separate crystals, two crystals belonging to different groups be dissolved together, the precipitate with the lime-salt, even in very dilute solutions, will form immediately or after a few seconds, in the state of an amorphous powder or of small thin laminæ, either isolated or arranged in stellated groups, according to the slowness of the precipitation,—in short, presenting all the characters of racemate of lime.—Racemic acid is

\* The term *symmetrical* must be understood throughout this Paper in the strict technical sense in which it is used in geometry.

not, however, a mere mixture of dextroracemic and levoracemic acid; every crystal of racemic acid, however small, gives, with a salt of lime, the distinguishing character of racemate of lime. In fact, the two acids cannot exist together in a solution, without combining and forming racemic acid. The same is the case with all the salts of these acids, excepting the double racemate of soda and ammonia already described, and the double racemate of soda and potash which is isomorphous with it.

*Dextroracemic and Levoracemic Acids.*—Dextroracemic acid is prepared by mixing a solution of dextroracemate of soda and ammonia with nitrate of lead, and treating the precipitate with sulphuric acid. The acid then separates, and may be obtained in crystals, the crystallization being facilitated by the presence of a slight excess of sulphuric acid. By slow evaporation, large, clear, crystals, of great beauty are obtained. These crystals are oblique rectangular prisms, with hemihedral modifications. The crystalline form is absolutely identical with that of tartaric acid obtained from ordinary cream of tartar; the acid has, likewise, the same composition, density and solubility, and, in short, is nothing but tartaric acid. It is convenient, however, to retain the name of *Dextroracemic acid*, when we wish to refer to the acid as one of the constituents of racemic acid, or to contrast its properties with those of levoracemic acid.

The preparation of levoracemic acid is precisely similar to that of the dextroracemic; it has likewise the same composition, density, and solubility. The crystalline forms of the two acids, however, are not *similar* but *symmetrical*,—so that, although their faces are precisely the same in form, number, and magnitude, they cannot be made to coincide by superposition. Moreover, tartaric or dextroracemic acid turns the plane of polarization of a luminous ray to the right; levoracemic acid turns it, by exactly the same quantity, to the left. For these reasons, levoracemic acid might also be called *Levolartaric acid*.

The crystals of both these acids are strongly *pyro-electric*; each crystal, when heated or cooled, becoming charged with opposite electricities at its two ends; but in either case, the direction of the positive and negative poles in a crystal of dextroracemic acid is precisely opposite to that which obtains in a crystal of levoracemic acid.

*Levoracemates and Dextroracemates.*—The relations of form, rotatory power, and chemical properties, already noticed in the dextroracemic and levoracemic acids are likewise found to the fullest extent in salts of these acids. All the chemical properties of the tartrates or dextroracemates are reproduced, even in the minutest details, in the corresponding levoracemates. To each tartrate there corresponds a levoracemate, differing from the former in nothing but in the position of the hemihedral facets and the direction of the

rotatory power. With regard to the angles of the faces, the absolute value of the rotatory power, the specific gravity, chemical composition, solubility, optical properties of double refraction, &c., the corresponding salts of the two groups are absolutely identical.

**Racemic acid and Racemates.**—It is well known that this acid was originally produced by an accidental alteration of tartaric acid in the manufactory of M. Kestner, at Thann. Its production on that occasion appears to have been due either to some particular and unobserved circumstance in the process of fabrication, or to some disease in the grapes from which it was formed; at all events, it has never been produced again, notwithstanding all the attempts which M. Kestner has made for that purpose. Its production is evidently due to some molecular alteration in tartaric or dextroracemic acid, by which a portion of that substance is converted into levoracemic acid. Now, as Biot has shewn that the rotatory action of tartaric acid on polarized light is diminished by reduction of temperature, it seemed possible that, by the action of intense cold, the direction of the rotatory power might be reversed, and thus the transformation into levoracemic acid effected. M. Pasteur has tried the experiment, but without any satisfactory result. For the present, then, the direct formation of racemic acid from tartaric is an unsolved problem; but this much is certain, that, when equal weights of dextroracemic and levo-racemic acids are dissolved in water, and the solution left to crystallize; the crystals obtained are perfectly homohedral, and present all the characters of racemic acid.—M. Pasteur has also carefully examined the crystalline forms of several salts of racemic acid,—particularly the neutral and acid racemates of soda and the racemate of antimony and potash—and finds them all perfectly homohedral.

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**On the Separation of some of the Acids of the Series  $(C H)_n O_4$ .**

**By Justus Liebig.**

For detecting small quantities of butyric or valerianic acid in a mixture of the two acids, and for separating one of them in a pure state fit for analysis, the following method may be advantageously pursued.

A portion of the acid mixture is first saturated with potash or soda, the remainder is then added to the neutral solution, and the whole distilled.

One of two results will then follow:

1. If the valerianic acid is present in quantity more than sufficient to saturate the whole of the alkali, the residue in the retort will contain no butyric acid, but only *pure valerianic acid*.

2. When the quantity of the valerianic acid is less, a proportional quantity of butyric acid remains behind in the retort, together with the whole of the valerianic acid; but the distillate is then free from the latter, and consists of *pure butyric acid*.



The quantity of the acid mixture to be neutralized with the alkali, must be regulated by the supposed quantity of valerianic acid present. For instance, if the proportion is calculated at 10 per cent,  $\frac{1}{10}$  of the mixture must be neutralized; and in a solution of valerianic acid containing 10 per cent of butyric acid, which it is required to separate,  $\frac{9}{10}$  of the acid mixture must be neutralized.

It is at once evident, that by a single distillation, one of the acids will always be obtained pure. Thus, either the distillate will consist of *pure butyric acid*, and the residue in the retort of a mixture of valerianic and butyric acids; or the distillate will contain both valerianic and butyric acid, and the residue will consist of *pure valerianic acid*.

By repeating this process of partial saturation and distillation, either with the mixed residues or the mixed distillates, as the case may be, a fresh portion of one or the other acid may again be obtained pure, till at last a complete separation is effected, such as can scarcely be accomplished by ordinary distillation.

Since butyric and valerianic acids have different boiling points, it may be supposed that the soda, inasmuch as it combines with one only of the acids, and that the least volatile—in this case the valerianic—will arrest the volatility of the latter at the temperature at which the former boils; and in a mixture of the two acids, if the valerianic acid is rendered permanent at the boiling point of the butyric, it is evident that the butyric acid may be distilled off in the pure state.

A mixture of valerianic acid with acetic acid, or of butyric acid with acetic acid, behaves under these circumstances in a totally different manner. Thus, if a mixture of this kind is partially neutralized with potash and then distilled, the acid which passes over, consists, not of acetic acid, as might be expected, but of the two other acids, although the boiling point of the acetic acid is upwards of 50° C. lower than the boiling point of butyric acid, and upwards of 70° lower than that of valerianic acid. This effect is due to the formation of an acid acetate, which does not appear to be decomposable by either of the other acids.

Valerianic acid added to a solution of neutral acetate of potash, dissolves immediately and in considerable quantity; but with acid acetate of potash, the valerianic acid remains swimming in oily drops on the surface, and does not appear to be more soluble therein than in pure water.

On distilling a solution of *neutral* acetate of potash to which valerianic acid has been added in excess, valerianic acid passes over, and the residue in the retort contains acid acetate, together with valerianate of potash. But if valerianic acid is added to *acid* acetate of potash and the mixture distilled, valerianic acid passes over, and the acid salt remains behind, free from valerianic acid.

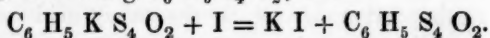
Butyric acid behaves in a precisely similar manner to valerianic acid.

Hence, when a mixture of butyric or valerianic acid with acetic acid is partially saturated with potash and distilled, either the whole of the acetic acid remains behind in the form of an acid salt, together with butyric acid, the distillate in this case being pure and free from acetic acid; or, acetic acid alone remains in the retort, and the distillate still contains a portion of acetic acid, which may be separated from the butyric or valerianic acid by repeating the process.

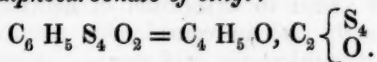
#### On the Derivatives of Xanthic Acid.

By H. Debus.\*

Dessains† has shown that, when iodine acts upon xanthate of potash, the potassium is removed in the form of iodide, and a compound formed containing  $C_6 H_5 S_4 O_2$ ; thus:



This product has been further examined by Debus; he, however, finds that it can be more conveniently formed from xanthate of lead. This salt is obtained by dissolving potash in common alcohol; adding to the solution a quantity of bisulphide of carbon and hydrated oxide of lead, corresponding to the quantity of potash used; and leaving the mixture at rest for 6 or 8 hours. At the end of that time, part of the oxide of lead is found to be transformed into sulphide, mixed with crystals of xanthate of lead, while another portion is dissolved by the potash. The black precipitate is separated by filtration, and water added to the filtered liquid, till a milkiness is produced. After a while, the liquid becomes clear and deposits xanthate of lead in long, silky crystals, containing  $C_6 H_5 O_2 S_4, Pb O$ . This salt is diffused through alcohol, and iodine added in small portions at a time, till the liquid acquires a permanent brown colour. The iodide of lead is separated by filtration, the liquid diluted with its own volume of water, and then left at rest for some hours, at a temperature of  $12^{\circ} C$ . The compound above-mentioned,  $C_6 H_5 S_4 O_2$ , is then deposited in small colourless prisms. This substance is regarded by Debus as *Bioxysulphocarbonate of ethyl*:



This substance is very soluble in absolute alcohol, and in ether; its solution gives no precipitate with acetate of lead, and with several other metallic solutions. When it is boiled with nitrate of silver, a precipitate of sulphur is formed. Chloride of mercury produces with it a white precipitate, which blackens at  $40^{\circ} C$ .; and bichloride of platinum gives, after a while, a brown, pulverulent precipitate.

When dry ammoniacal gas is passed into an alcoholic solution of bioxysulphocarbonate of ethyl, the liquid gradually becomes turbid

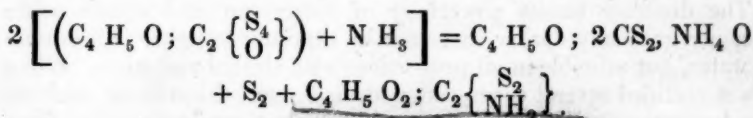
\* Ann. Ch. Pharm. LXXII, 1. † Ann. Ch. Phys. [3] XX, 496.



and deposits long needles of sulphur. If the filtered liquid be then evaporated in vacuo, a saline residue is obtained, containing a mixture of *xanthate of ammonia*, and a new substance to which Debus gives the name of *Xanthogenamide*. These substances are separated by digestion in ether, which dissolves the latter only.

The xanthogenamide remains, after the evaporation of the ether, in the form of a yellow oil, which ultimately solidifies in a crystalline mass. It is purified, by solution in a small quantity of alcohol, from which it crystallizes, on evaporation, in splendid, rhomboidal prisms, often of considerable size. These crystals fuse at about  $30^{\circ}$ ; they are slightly soluble in water, but dissolve, in all proportions, in alcohol and ether. The solution is neutral, and gives no precipitate with nitrate of silver, acetate of lead, sulphate of copper, or baryta-salts; but it precipitates bichloride of platinum and corrosive sublimate. The oxides of mercury, silver, and lead, and likewise carbonate of silver, decompose this substance, producing a sulphide of the metal, and a substance which attacks the eyes powerfully, and has an odour like that of acrolein. Concentrated sulphuric acid readily dissolves xanthogenamide; water precipitates it again without alteration. Nitric acid attacks it strongly, forming a peculiar acid. Potash and baryta-water, at a boiling heat, resolve it into alcohol and hydro-sulphocyanic acid. Ammonia at  $150^{\circ}$  C., produces carbonic acid, hydrosulphocyanic acid, and a number of fœtid products.

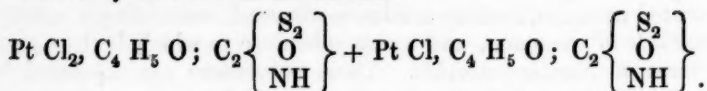
The composition of xanthogenamide is,  $C_6H_7O_2S_2N$ . In its formation, 2 eq. bioxysulphocarbonate of ethyl and 2 eq. ammonia are resolved into 1 eq. xanthate of ammonia, 2 eq. sulphur, and 1 eq. xanthogenamide:



When an alcoholic solution of xanthogenamide is mixed with bichloride of platinum, a yellow, crystalline precipitate separates, after a few minutes, and the filtered liquid continues for some days to deposit crystalline scales. By analysis, these crystals gave the following results:

	Eq.	Calculated.		Found.		
				I.	II.	III.
Carbon . .	12	72	14.01	13.97	13.39	—
Hydrogen .	14	14	2.72	2.69	2.72	—
Oxygen . .	4	32	6.24	—	—	—
Sulphur . .	4	64	12.46	—	13.35	—
Nitrogen .	2	28	5.45	—	—	—
Platinum .	2	197.4	38.43	38.04	38.26	37.85
Chlorine .	3	106.2	20.69	19.08	23.30	—
		513.6	100.00			

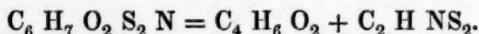
Hence may be deduced the formula :



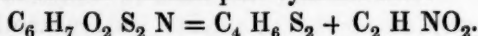
The mother-liquid separated from these precipitates is very dark-coloured, and, when evaporated, gives off vapours of hydrochloric acid, and yields a brown oil, which gradually volatilizes, together with the water and alcohol vapours; there then remains a brown substance, possessing the properties of sulphide of platinum, together with a white crystalline body, which was recognized as sal-ammoniac.

The above-mentioned platinum compound is insoluble in alcohol, ether, and water. Strong sulphuric acid has no action upon it in the cold, and but a slight action when heated. Potash, nitric acid, and hydrochloric acid produce no alteration in it; but *aqua regia* dissolves it with facility. At 120° C. it begins to decompose, evolving a fetid oil.

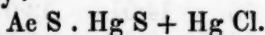
Potash and baryta transform xanthogenamide into alcohol and a sulphocyanide of the metal: the reaction consists in simple decomposition.



When xanthogenamide is submitted to dry distillation, mercaptan and vapours of cyanic acid are given off. If the distillation is performed at 152° C., the residue contains pure cyanuric acid:



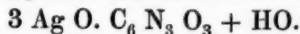
The distillate smells powerfully of mercaptan and cyanic acid; becomes gradually darker in colour by exposure to light, is insoluble in water, but miscible in all proportions with alcohol and ether. When it was rectified several times, after drying over chloride of calcium, the boiling point did not become fixed, but gradually rose from 50° to 230° C. The portions which first went over were colourless; the last had a strong yellow colour. Both portions had a very feeble alkaline reaction, and, when dissolved in alcohol, gave scanty, white precipitates with silver, copper, and lead salts; but with corrosive sublimate, a copious, bulky precipitate, which, when left for some time in contact with the mother-liquid, was converted into crystalline laminae. By analysis, it was found to be a compound of mercaptide and chloride of mercury:



As a check on the preceding results, the cyanuric acid produced by the distillation of the xanthogenamide was mixed, in the state of a hot dilute solution, with nitrate of silver, and dilute ammonia was added as long as a precipitate continued to form. The salt thus obtained evolved ammonia when heated, and acquired a violet colour. Potash, in the cold, had no action upon it. Analysis gave the following results:

	Eq.	Calculated.		Found.	
				I.	II.
Carbon . . . .	6	36	7·85	7·6	7·4
Hydrogen . . . .	1	1	0·21	0·3	0·3
Oxygen . . . .	7	56	12·27	—	—
Nitrogen . . . .	3	42	9·10	8·98	—
Silver . . . .	3	324	70·57	70·25	70·41
		459	100·00		

Hence the salt is a tricyanurate of silver with 1 eq. water :



Liebig and Wöhler found in the same salt, dried at 300° C. :

	Liebig.		Wöhler.
Carbon . . . .	8·13	7·82	8·4
Hydrogen . . . .	0·13	0·18	0·12
Silver . . . .	70·00	71·10	70·52

#### On Caffeine.

By Fr. Rochleder.\*

When chlorine gas is passed into a thick magma of crystals of caffeine, the liquid becomes heated, and a solution is obtained containing four substances: hydrochloric acid, the hydrochlorate of an alkaloid, a weak acid, and a very volatile product which could not be procured in sufficient quantity or sufficiently pure for analysis. On heating the solution in the water-bath, the excess of chloride is driven off, together with the hydrochloric acid and the volatile product, which is remarkable for its offensive odour; it irritates the eyes and produces an intolerable pain in the head. As soon as the liquid is evaporated to a third of its original bulk, it begins to deposit crystals, the quantity of which gradually increases. When the crystals no longer appear to form, the liquid is left to cool, and the crystals are taken out. They are then washed with cold water, in which they are nearly insoluble, and then exhausted in boiling absolute alcohol, which does not dissolve them at all. They may also be recrystallized from boiling water. They are colourless and transparent, contain no water that can be driven off at 100°, redden litmus slightly, and, at the same time, acquire a slight rose-colour by the action of the ammonia contained in the blue litmus-paper. With baryta, potash, and soda, this substance forms compounds of a dark violet colour. When a solution of either of these bases is brought in contact with the above crystals, the latter immediately assume a violet colour, while the liquid remains colourless. This colouring is but transient if the base is in excess, but tolerably persistent in the case of an excess of acid.

\* Ann. Ch. Pharm. LXXI, 1.

To this acid, Rochleder gives the name of *amalic acid*, (from *αμαλος*, weak), to denote its feebly acid nature, and likewise the slight affinity by which its elements are held together, and the consequent facility with which it is decomposed.

Ammoniacal vapours impart to amalic acid a red colour, faint at first, but gradually changing to deep violet. The resulting compound dissolves in water, forming a solution of the colour of murexide. This solution, however, does not yield crystals of murexide; but Rochleder has succeeded in obtaining a crystalline substance from it, the description and analysis of which will be given in a future memoir. With ferrous salts and ammonia, amalic acid forms an indigo-coloured solution.

Amalic acid fuses when heated, becoming first yellow, then red, afterwards brown, and volatilizes, leaving scarcely a trace of carbon, but giving off ammonia, and forming an oil and a crystallized compound. The solution of amalic acid, placed upon the skin, produces red stains, having a disagreeable odour, like those produced by alloxan. It reduces silver salts, throwing down black flakes of metallic silver, just as alloxantine does. When boiled with nitrate of silver and nitric acid, it is decomposed, without the formation of even a trace of chloride of silver; hence amalic acid contains no chlorine. When heated with nitric acid, it evolves red vapours, and is converted into a new crystalline body.

The composition of amalic acid is  $C_{12} H_7 N_2 O_8$ , as appears from the following analysis :

	Eq.	Calculation.		Experiment.			
		72	42·10	41·83	42·04	42·04	—
Carbon . .	12	72	42·10	41·83	42·04	42·04	—
Hydrogen .	7	7	4·09	4·35	4·17	4·27	4·18
Nitrogen .	2	28	16·37	—	16·63	16·30	—
Oxygen .	8	64	37·44	—	37·16	37·39	—
		171	100 00	100·00		100·00	

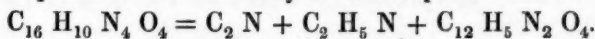
When the mother-liquid decanted from the crystals of amalic acid is evaporated to a fourth of its original volume, to expel the greater part of the hydrochloric acid, it solidifies, on cooling, in a thick, crystalline mass, which may be separated from the adhering liquid by pressure between linen, and afterwards crystallized from boiling water or alcohol. In this manner, a crystalline mass is obtained, greasy to the touch, and consisting of large, laminated crystals. The solution of this substance gives, with chloride of platinum, a copious yellow precipitate, and, with nitrate of silver, an abundant precipitate of chloride of silver. The crystals consist of the hydrochlorate of a new base. To analyze this base, Rochleder converted it into a platinum salt, by mixing the mother-liquid above-mentioned with bichloride of platinum, collecting the yellow precipitate on a filter, and dissolving it in boiling water: the solution, on cooling, yielded

very brilliant, yellow, granular crystals of the double salt. This salt was found by analysis to contain :

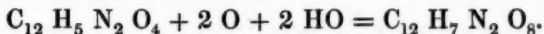
Carbon . . . .	4.87	4.86	—	—
Hydrogen . . . .	2.49	2.49	2.42	—
Platinum . . . .	41.42	41.43	41.61	41.06

agreeing with the formula :  $C_2 H_4 N. Cl H + Pt Cl_2$  ; whence the formula of the new base is :  $C_2 H_4 N$ . To this base, Rochleder\* gave the name, *Formylne*. Subsequently, however, on repeating the analysis, he found the per centage of carbon to be 5.2, and of hydrogen 2.62. These numbers agree better with the formula :  $C_2 H_5 N$ . which is that of *Methamylne*, discovered by Wurtz. Moreover, the properties of the so-called formylne are identical with those of methamylne ; whence Rochleder concludes that methamylne is one of the products of the action of chlorine on caffeine.

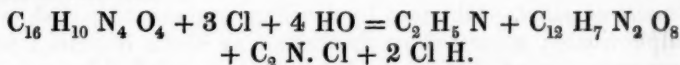
The composition of caffeine may be thus expressed :



By the action of chlorine in presence of water, the cyanogen is decomposed ; the methamylne is obtained in the form of a hydrochlorate ; and the group,  $C_{12} H_5 N_2 O_4$ , takes up 2 eq. oxygen, and 2 eq. water, and forms amalic acid :



That cyanogen is really contained in caffeine, is shown, according to Rochleder, by its behaviour with alkalis. Caffeine, treated with strong potash-ley or soda-lime, yields cyanide of potassium or sodium, whereas quinine, cinchonine, morphia, and piperine, when similarly treated, yield not a trace of cyanogen. The volatile, tear-exciting substance above-mentioned, is considered by Rochleder to be produced by the action of chlorine on the cyanogen of the caffeine, at the moment when the cyanogen is separated from the other elements of that substance. M. Gerhardt,† however, remarks that it is highly improbable that cyanogen should be actually set free by the action of chlorine on a liquid containing a cyanide, or, indeed, on any cyanogen compound whatever : accordingly he is of opinion that the volatile substance just mentioned is *chloride of cyanogen*. According to this view, the action of chlorine on caffeine will be represented as follows :



If the action of the chlorine be continued further, a product is obtained from the amalic acid, closely resembling cholesterine. This is the substance which Stenhouse obtained by the action of nitric

\* Ann. Ch. Pharm. LXXIII, 56.

† Compt. Rend. des Trav. en Chim. Janvier, 1850, 25.

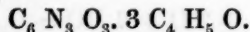


acid on caffeine or theine, and to which he gave the name *Nitrotheine*. This name, however, is inadmissible, inasmuch as the substance in question contains no nitrogen, and is formed by the action of chlorine as well as by nitric acid. Rochleder calls it *Cholestrophane*. It contains carbon, 42.15, hydrogen, 4.28, nitrogen, 19.56, and is expressed by the formula:  $C_{10} H_6 N_2 O_6$ . When boiled with potash, it evolves a volatile alkali, probably methamylene, and forms carbonate and oxalate of potash.

**On the Compounds of Cyanuric and Cyanic Acid with the Oxides of Ethyl, Methyl, and Amyl, and on the products resulting therefrom, viz.: Acetyl- and Metacetyl-Urea, and Methylamine, Ethylamine, and Valeramine.**

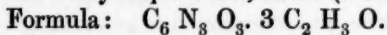
By Adolph Wurtz.\*

1. *Cyanurates of ethyl and methyl*.—Cyanurate of ethyl is obtained by distilling alkaline cyanurate of potash with sulphovinate of potash over an oil-bath. The product condenses in the neck of the retort and in the receiver, in the form of a crystalline mass; it may be purified by repeated solution in alcohol, from which it separates on cooling, in very brilliant prismatic crystals. Cyanuric ether fuses at  $85^{\circ} C.$  forming a colourless liquid which is heavier than water. Boils at  $276^{\circ}$ , distilling over completely, and without the least decomposition. Vapour-density = 7.4 by experiment, 7.37 (4 vol.) by calculation. Formula:



Sparingly soluble in water, but easily dissolved by alcohol and common ether. This compound is likewise formed, together with cyanate of ether (which boils at  $60^{\circ} C.$ ) on distilling cyanate of potash with the sulphovinate. The two ethers may be easily separated by distillation; and the cyanuric ether which remains in the retort, forms, after purification, even finer and more regular crystals than those obtained by the first described process.

*Cyanurate of methyl*.—Obtained by distilling cyanurate or cyanate of potash with sulphomethylate of potash. When purified by repeated crystallization from alcohol, it forms small, colourless, prismatic crystals, which fuse at  $140^{\circ} C.$ , and volatilize at  $295^{\circ}$ . Vapour-density = 5.98 by experiment, 5.94 (4 vol.) by calculation.

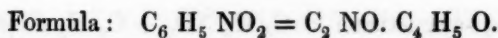


The composition of these ethers verifies Liebig's statement, that cyanuric acid is terbasic.

*Cyanate of ethyl*.—Obtained by distilling cyanate of potash with the sulphovinate; separated by distillation as above described from the cyanurate formed at the same time. When purified by repeated distillation over chloride of calcium, it forms a light, highly refractive liquid, of extremely penetrating odour, and exciting a copious flow of tears. Lighter than water. Vapour-density = 2.4 (4 vol.).

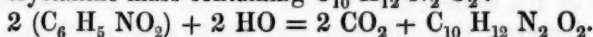
\* Ann. Ch. Pharm. LXXI, 326; Compt. Rend. XXVI, 368; XXVII, 241 (1848); XXVIII, 322 and 323; XIX, 169, 186 and 203 (1849).



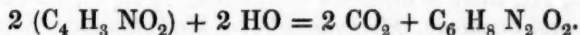


When cyanic ether is mixed with liquid ammonia, it dissolves, with evolution of heat; and on evaporation, beautiful prismatic crystals are obtained, consisting of  $\text{C}_6 \text{H}_8 \text{N}_2 \text{O}_2$ , that is to say, cyanic ether *plus* ammonia. They fuse easily, and dissolve with facility in water and alcohol.

In contact with water, cyanic ether gives off carbonic acid, and forms a crystalline mass containing  $\text{C}_{10} \text{H}_{12} \text{N}_2 \text{O}_2$ :



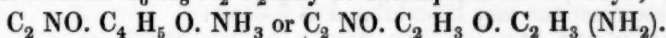
*Cyanate of methyl* is prepared and purified by methods precisely similar to those just described for cyanic ether. It is a volatile liquid, which, with ammonia, forms a crystalline compound  $= \text{C}_4 \text{H}_6 \text{N}_2 \text{O}_2$ , and in contact with water is resolved into carbonic acid, and a crystalline compound isomeric with the ammonia-compound of cyanate of ethyl.



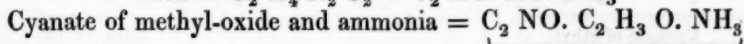
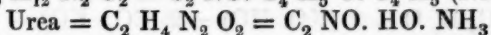
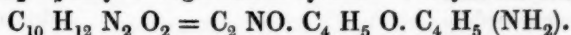
The compounds thus formed are to a certain degree analogous in composition to urea. For, urea with 1 eq. methylene,  $\text{C}_2 \text{H}_2$ , or its elements, gives  $\text{C}_4 \text{H}_6 \text{N}_2 \text{O}_2$ , which is the body corresponding to urea in the acetic acid series. This is the substance formed by the action of ammonia on cyanate of methyl. Further, if to this formula we again add the elements of methylene,  $\text{C}_2 \text{H}_2$  we obtain  $\text{C}_6 \text{H}_8 \text{N}_2 \text{O}_2$  the urea of the metacetyl series. This compound may be formed in either of the two ways mentioned above. By treating cyanic ether with water, we obtain the analogue of urea in the valerianic acid series. Two other bodies of this series might be formed from cyanate of amyl.

The compound formed by the union of cyanic ether with ammonia, and that which is produced by the action of water on cyanate of methyl are not, however, identical, but merely isomeric. The former appears to be analogous to urea; while the latter appears rather to belong to the class of *Amethanes*, that is to say, compounds of ethers with amidogen.

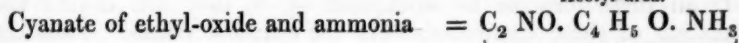
The formula  $\text{C}_6 \text{H}_8 \text{N}_2 \text{O}_2$  may be decomposed in two ways; viz.:



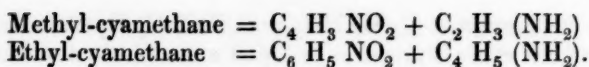
The first of these formulæ is that of urea, with 1 eq. water replaced by 1 eq. ether; the second is that of a compound of cyanate of methyl with methylamine (*vide infra*). Similarly, the compound  $\text{C}_{10} \text{H}_{12} \text{N}_2 \text{O}_2$  may be regarded as cyanate of ethyl with ethylamine.



Acetyl-urea.



Metacetyl-urea.

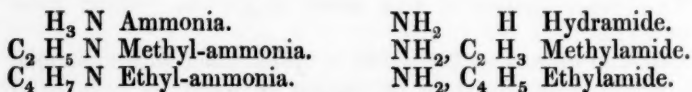


## ETHYLAMINE AND METHYLAMINE.

*Formation.*—The ammonia-compounds form a sort of connecting link between organic and inorganic compounds. Indeed ammonia would no doubt be regarded as an organic base, and the simplest and strongest of the whole class, were it not that it contains no carbon. Possibly, however, this difference may not be of so much importance as it has hitherto been thought; for Wurtz has succeeded in forming organic compounds from this alkali, by adding to it the elements of methylene,  $\text{C}_2 \text{H}_2$ , or etherine,  $\text{C}_4 \text{H}_4$ , without depriving it of its strong basic properties, or even of its smell.

If to the elements of ammonia  $\text{NH}_3$ , there be added the elements of 1 eq.  $\text{C}_2 \text{H}_2$ , there is formed a compound,  $\text{C}_2 \text{H}_5 \text{N}$ , which may be called *Methyl-ammonia*, *Methylamide*, or *Methylamine*. On adding to the elements of ammonia, the elements of 1 eq.  $\text{C}_4 \text{H}_4$ , there results the compound,  $\text{C}_4 \text{H}_7 \text{N}$ , which may be called *Ethyl-ammonia*, *Ethylamide*, or *Ethylamine*.

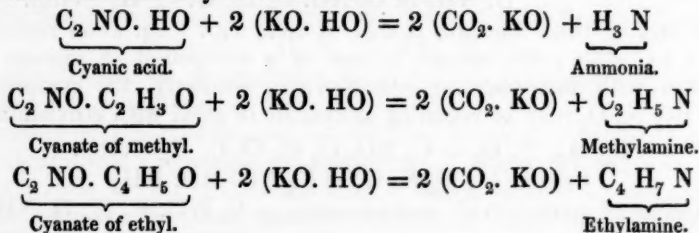
The compounds  $\text{C}_2 \text{H}_5 \text{N}$  and  $\text{C}_4 \text{H}_7 \text{N}$  may be regarded either as methyl-ether  $\text{C}_2 \text{H}_3 \text{O}$ , and common ether  $\text{C}_4 \text{H}_5 \text{O}$ , in which 1 eq. oxygen is replaced by 1 eq. amidogen  $\text{NH}_2$ , or as ammonia, in which 1 eq. hydrogen is replaced by methyl,  $\text{C}_2 \text{H}_3$ , or ethyl,  $\text{C}_4 \text{H}_5$ . The relations between these bodies and ammonia may be exhibited as follows:



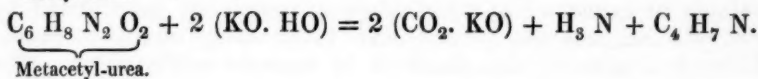
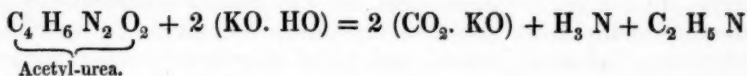
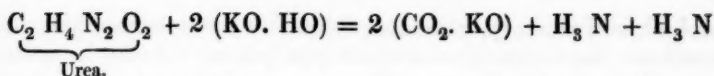
These bases may be formed in three ways:

1. By the action of potash on the *Cyanic ethers*.
2. By the action of potash on the *Cyanuric ethers*.
3. By the action of potash on the *Ureas*.

These reactions may be exhibited as follows:



If all these formulæ be multiplied by 3, they will exhibit the formation of these compounds from the cyanuric ethers. From the ureas they are formed as follows:



*Methylamine.*—When cyanurate of methyl is boiled with excess of caustic potash, and the evolved vapours are passed through a condensing tube into water, a highly caustic liquid is obtained, which smells strongly of ammonia, but does not contain a trace of that alkali; it is an aqueous solution of methylamine. On saturating this solution with hydrochloric acid, and evaporating to dryness, a residue is obtained which dissolves readily in warm absolute alcohol. On cooling, the hydrochlorate of methylamine crystallizes out in splendid laminæ, which are iridescent as long as they remain in the liquid, and assume a mother-of-pearl aspect when dry. From the hydrochlorate, the base may be obtained in the free state by a process exactly similar to that adopted for the preparation of ammonia, viz., by heating the dry salt with quick lime in a flask provided with a gas-delivery tube. The methylamine is then evolved in the gaseous form, and may be collected over mercury.

Methylamine is gaseous at ordinary temperatures; at 0° C. it condenses to a very mobile liquid. Specific gravity of the gas, 1.13 by experiment, 1.075 by calculation. Water, at 12°, absorbs 1040 times its volume of gaseous methylamine, a larger quantity than of any other known gas; at 25°, the volume absorbed is 950 times that of the water.

The gas resembles ammonia in the following respects. It is rapidly absorbed by charcoal; turns reddened litmus paper blue; forms dense white fumes with hydrochloric acid; absorbs an equal volume of hydrochloric acid gas, and half its volume of carbonic acid. It is distinguished from ammonia by taking fire when brought in contact with the flame of a candle, and burning with a yellowish flame.

It is decomposed when heated with potassium, cyanide of potassium being formed and hydrogen set free. This furnishes a good method of analysis.

The solution has the strong smell of the gas itself; its taste is caustic and burning. Iodine introduced into this solution is converted into a garnet-coloured powder, and the liquid, which scarcely becomes coloured, holds in solution hydriodate of methylamine,  $\text{I H. C}_2 \text{H}_5 \text{N}$ . The red insoluble substance is the compound analogous to iodide of nitrogen.

The salts of magnesia, alumina, manganese, iron, bismuth, uranium,

tin, lead, and mercury, are precipitated by methylamine just as by ammonia. Zinc-salts give a white precipitate, soluble in a large excess of the alkali.—Copper-salts are precipitated bluish-white; an excess of methylamine dissolves the precipitate, forming a deep blue solution. Cadmium, cobalt, and nickel salts give precipitates not soluble in excess.—Nitrate of silver is completely precipitated by methylamine, the precipitated oxide being easily soluble in excess. Chloride of silver is also dissolved by aqueous methylamine. The solution, when left to spontaneous evaporation, deposits a black powder, analogous to fulminating silver, but not exploding either by heat or by percussion.—Chloride of gold gives a brownish-yellow precipitate, easily soluble, and forming an orange-yellow solution.—Chloride of platinum gives a yellow crystalline precipitate, composed of  $\text{Cl H. C}_2 \text{H}_5 \text{N. Pt Cl}_2$ .

*Hydrochlorate of Methylamine* gave by analysis the following numbers, agreeing with the formula  $\text{Cl H. C}_2 \text{H}_5 \text{N}$ .

	Eq.	Calculated.		Experiment.
Carbon . . . .	2	12	17.7	17.4
Hydrogen . . . .	6	6	8.8	8.7
Chlorine . . . .	1	35.5	52.5	52.2
Nitrogen . . . .	1	14	21.0	21.7
		67.5	100.0	100.0

*Chloroplatinate of Methylamine*, which crystallizes in beautiful golden-yellow scales, was also analysed, and gave carbon 5.3, hydrogen 2.8, chlorine 44.4, platinum 41.4, (nitrogen not determined), agreeing with the formula,  $\text{Cl H. C}_2 \text{H}_5 \text{N. Pt Cl}_2$ .

*Ethylamine*.—The hydrochlorate of this base is prepared and purified by processes precisely similar to those described for methylamine; and the base itself is likewise obtained by dry distillation of the hydrochlorate with quick-lime. But as ethylamine is easily condensed, and is liquid at ordinary temperatures, the gas-delivery tube is made to pass into a receiver surrounded with a freezing mixture.

Light, very mobile, and perfectly transparent liquid. Begins to boil at  $18^\circ \text{C}$ . If poured upon the hand, it volatilizes immediately, producing a sensation of intense cold. It diffuses a highly penetrating ammoniacal odour. Its causticity may be compared with that of potash. Blues reddened litmus-paper strongly. Forms dense white fumes with hydrochloric acid. Each drop of the acid poured into it produces a hissing noise. Caustic potash or baryta may be left in contact with the base, at ordinary temperatures, without producing any change. In contact with a burning body, ethylamine takes fire and burns with a bluish flame.

Ethylamine is miscible with water in all proportions, and the solu-

tion possesses exactly the same properties as that of methylamine, excepting that it dissolves hydrated oxide of copper less readily, and does not precipitate bichloride of platinum.

When a solution of ethylamine is mixed with oxalic ether, the mixture soon becomes turbid, alcohol being formed, and delicate crystals being deposited, which consist of a compound bearing the same relation to oxamide that methylamine bears to ammonia. This compound is *Ethyl-oxamide*,  $C_6 H_6 N_2 O_2$ .

The composition of anhydrous ethylamine is expressed by the formula  $C_6 H_7 N$ , as appears from the following analysis :

	Eq.	Calculated.		Experiment.	
Carbon . . .	4	24	53·3	53·4	—
Hydrogen . . .	7	7	15·5	15·9	—
Nitrogen . . .	4	14	31·2	30·9	31·3
		45	100·0	100·2	

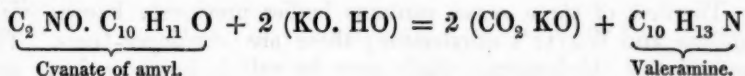
*Hydrochlorate of Ethylamine* crystallizes in laminæ; fuses at  $100^0$ , and solidifies in a crystalline mass on cooling; its composition is  $Cl H. C_4 H_7 N$ .

	Eq.	Calculated.		Experiment.	
Carbon . . .	4	24	29·4	28·9	29·4
Hydrogen . . .	8	8	9·8	9·9	9·9
Nitrogen . . .	1	14	17·2	17·5	—
Chlorine . . .	1	35·5	43·6	43·7	—
		81·5	100·0	100·0	

*Chloroplatinate of Ethylamine*.—Golden-yellow scales, soluble in water. The analysis of this salt gave in 100 parts: carbon 9·5, hydrogen 3·2, chlorine 42·4 and 42, platinum 39·2 and 39, agreeing with the formula,  $Cl H. C_4 H_7 N. Pt Cl_2$ .

*Valeramine*  $C_{10} H_{13} N$ .—Formed from ammonia, by the addition of  $C_{10} H_{10}$ , or by the substitution of 1 eq. of amyl,  $C_{10} H_{11}$ , for 1 eq. of hydrogen.

Cyanate of amyl, prepared by distilling cyanate of potash with sulphamylate of potash, yields this base when decomposed by caustic potash :



The valeramine distils over, and may be condensed in a receiver containing water. The alkaline solution, neutralized with hydrochloric acid, yields the hydrochlorate; and this, when purified, dried and distilled with caustic lime, yields anhydrous valeramine.

Valeramine is liquid at ordinary temperatures, has a burning,

bitter taste, and a strong ammoniacal odour. It is soluble in water. The solution precipitates copper-salts, and an excess redissolves the precipitate, forming a deep blue solution, less readily, however, than ethylamine, methylamine, or ammonia. With nitrate of silver it gives a brownish precipitate, soluble in excess. Valeramine dissolves chloride of silver, but less easily than ammonia.

*Hydrochlorate of Valeramine*,  $\text{Cl H. C}_{10} \text{H}_{13} \text{N}$ , crystallizes in scales, unctuous to the touch, and soluble in water and alcohol.

	Eq.	Calculated.		Experiment.
Carbon . . .	10	60	48.5	48.2
Hydrogen . . .	14	14	11.3	11.4
Chlorine . . .	1	35.5	28.7	28.3
Nitrogen . . .	1	14	11.5	—
		123	100.0	

*Chloroplatinate of Valeramine*.—Golden-yellow scales, soluble in water. Analysis gave 32.4 platinum, 36 chlorine, 20.4 carbon, 4.8 hydrogen, agreeing with the formula  $\text{Cl H. C}_{10} \text{H}_{13} \text{N. Pt Cl}_2$ .

Dr. Hofmann\* has lately shown that *two* and even *all three* of the hydrogen-atoms in ammonia may be replaced by organic radicals, ethyl, methyl, &c., and has thus obtained new volatile compounds, resembling ammonia, and possessing very strong basic properties. The following table exhibits the composition of these bases :

$\text{C}_4 \text{H}_5 = \text{Ae} = \text{Ethyl}$		
$\text{C}_{10} \text{H}_{11} = \text{Ayl} = \text{Amyl}$		
$\text{C}_{12} \text{H}_5 = \text{Pyl} = \text{Phenyl}$		
(1) $\left. \begin{array}{l} \text{H} \\ \text{H} \\ \text{Pyl} \end{array} \right\} \text{N}$	$\left. \begin{array}{l} \text{H} \\ \text{H} \\ \text{Pyl} \end{array} \right\} \text{N}$	$\left. \begin{array}{l} \text{H} \\ \text{H} \\ \text{Ae} \end{array} \right\} \text{N}$
Aniline or Phenamine	Phenamine	Ethylamine
(2) $\left. \begin{array}{l} \text{H} \\ \text{Ae} \\ \text{Pyl} \end{array} \right\} \text{N}$	$\left. \begin{array}{l} \text{H} \\ \text{Ayl} \\ \text{Pyl} \end{array} \right\} \text{N}$	$\left. \begin{array}{l} \text{H} \\ \text{Ae} \\ \text{Ae} \end{array} \right\} \text{N}$
Ethylphenamine	Amylophenamine	Diethylamine
(3) $\left. \begin{array}{l} \text{Ae} \\ \text{Ae} \\ \text{Pyl} \end{array} \right\} \text{N}$	$\left. \begin{array}{l} \text{Ae} \\ \text{Ayl} \\ \text{Pyl} \end{array} \right\} \text{N}$	$\left. \begin{array}{l} \text{Ae} \\ \text{Ae} \\ \text{Ae} \end{array} \right\} \text{N}$
Diethylphenamine	Ethylamylophenamine	Triethylamine

The first of these series contains bodies previously known, viz.: aniline and Wurtz's ethylamine; these are *Amidogen-bases*. The second and third series, which may be called *Imidogen-bases* and *Nitrile-bases*, are new.

\* Ann. Ch. Pharm. LXXIII, 91.



THE  
QUARTERLY JOURNAL  
OF THE  
CHEMICAL SOCIETY.

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Anniversary Meeting, March 30, 1850.

THE PRESIDENT in the Chair.

*The following Annual Report was read by the President.*

WE are now arrived at the Tenth Anniversary of this Society; and the steady, though not rapid, advance which has marked its existence from the formation to the present time, must be considered as auguring well for its prosperity and permanence.

It appears by the last Report, that the Society then consisted of one hundred and twelve resident and one hundred and twelve non-resident Members, three Associates, and nine Foreign Members. In the present session, there have been elected twelve Members, of whom four are resident, and eight non-resident; three resident, and three non-resident Members have withdrawn, and we have lost two Members by death. Twelve Foreign Members have been elected, comprehending, as you cannot fail to observe, names of philosophers of the highest reputation.

The Foreign Members elected are:

MM. Boussingault, Chevreul, Gay-Lussac, Gmelin, Kopp, Laurent, Mitscherlich, Pelouze, Regnault, Rose, Thénard, and Wöhler.

The Society, therefore, now consists of

243	{	101 Resident Members
		120 Non-resident Members
		2 Associates
		20 Foreign Members.

I have already stated that we have lost two non-resident Members by death: namely, Mr. William Crawhall and Colonel Thomas

Moody. The former gentleman was a native of Allendale, in Northumberland, where he was born in 1784. After a school education under a neighbouring clergyman, he was placed in his father's office, who was agent to the lead mines of Sir Thomas Blackett. In this situation, he paid considerable attention to the stratification of the rocks of the lead-mining district; and of the mines he drew plans and sections, so as to acquire an accurate knowledge of the mineral products of the country, the results of which were highly beneficial to Colonel Beaumont and to himself.

In 1812, on the death of his father, Mr. Crawhall succeeded him as superintendent of the mines of Colonel Beaumont, and his attention was naturally drawn to the process of *lead smelting*, as the operation was then conducted, and the injurious effects which the vapour escaping produced on vegetation, and the loss of metal which attended it. To remedy these evils, he constructed long horizontal chimnies, one of which is two and a half miles in length, and his plans were attended with great success.

It may be stated, without any diminution of the credit due to Mr. Crawhall, that the same plan had been previously proposed by Bishop Watson,\* but it does not appear that it was ever carried into effect.

In the year 1845, owing to the declining state of his health, he retired to his house, near Hexham, where he died on the 28th of March, 1849.

Colonel Moody obtained his commission in the corps of Royal Engineers while in the West Indies, where he was employed on active service. He was for many years engaged in the Colonial Office, and, subsequently, held the appointment of Inspector of Gunpowder at Waltham Abbey.

The following are the titles and names of the authors of the several Memoirs which have been read before the Society, since the last Anniversary.

1. "Analysis of Gold Dust from the Coast of California:" by E. F. Teschemacher.

2. "Analysis of the Thames Water at Greenwich:" by Edward T. Bennet.

3. "Analysis of a Mineral Water from the Neighbourhood of Bristol:" by Thornton J. Herapath.

4. "On the Sulphites of Potash, Chromium, Lithia, and Bismuth:" by Joseph Danson.

\* Watson's Essays, Vol. III, Essay 8.

5. "Notes on a Singular Substance resulting from Cloves:" by Dr. R. Scott.
6. "An Analysis of Plate Glass:" by Messrs. J. E. Mayer and J. S. Brazier.
7. "Researches on the Amyl Series:" by H. Medlock.
8. "On the Carbonate of Alumina:" by J. S. Muspratt.
9. "On the Manufacture of Soda, and the Composition of Salt-cake, Black-ash, Soda-ash, and Soda-waste:" by Frederick Muspratt and Joseph Danson.
10. "On Chromate of Copper:" by H. Sugden Evans.
11. "On the Quantitative Estimation of Cyanogen in Analysis:" by Charles Heisch.
12. "Examination of some Slags from Copper-smelting Furnaces:" by Frederick Field.
13. "On the Relative Expansion of Mixtures of Alcohol and Water, under the influence of a certain rise of Temperature, and on a New Instrument for taking the Specific Gravities of the same:" by G. H. Makins.
14. "On some New Acids contained in the Oil of the *Bassia Latifolia*:" by T. F. Hardwick.
15. "Researches on Strychnia:" by E. C. Nicholson and F. A. Abel.
16. "On the Isolation of Organic Radicals:" by E. Frankland.
17. "On a New Series of Organic Bodies, containing Metals and Phosphorus:" by E. Frankland.
18. "Researches on the Volatile Organic Bases:" by A. W. Hofmann.
19. "On the Water of the Dead Sea:" by Thornton J. Herapath and William Herapath.
20. "Analysis of the Well Water at the Royal Mint:" by W. T. Brande.
21. "On Titanium:" by Prof. Wöhler.
22. "Continuation of the Researches on the Volatile Organic Bases:" by A. W. Hofmann.
23. "Analysis of a Deep Well Water:" by J. Mitchell.
24. "On the Prevention of Incrustation in Steam Boilers:" by J. Anderson.
25. "On the Action of Sulphur on the Pentachloride of Phosphorus:" by J. R. Gladstone.
26. "On the Gases Eliminated from Sewers:" by M. Seanlan and J. Anderson.

27. "On the Action of Arsenious Acid on Albumen:" by J. B. Edwards.
28. "On the Composition of Mesitolole:" by M. Cahours.
29. "On the Identity of Bisulphethylic and Hyposulphethylic Acids, and of Bisulphimethylic and Hyposulphamethylic Acids:" by J. S. Muspratt.
30. "On some of the Salts of Carbonic Acid:" by M. N. Samuelson.
31. "Observations on Etherification:" by Thomas Graham.
32. "On a Natural Alloy of Copper and Silver from Chili:" by Frederick Field.
33. "Researches on the Organic Radicals:" by E. Frankland.
34. "On some Salts of Chromic Acid:" by J. Danson.
35. "On the Relations of Animal and Vegetable Life:" by R. Warington.
36. "On the Precipitation of the Colouring Matter of Sugar by a Metallic Oxide:" by Henry Warburton.
37. "On the Relations between Chemical Composition, Boiling Point, and Specific Volume:" by Hermann Kopp.
38. "On the Composition of the Ashes of the Cactus:" by Frederick Field.
39. "On the Application of Liquid Diffusion to Produce Decomposition:" by Thomas Graham.

The laborious investigations of which the above-named communications are the results, it would be a pleasing task to dilate upon; but such an occupation of your time would be needless, since most, if not all of them, are, or will be printed in your Journal, which I trust will ever be regarded as indicative of the zeal and ability of the Members of this Society.

It will now be proper for me to state the various specimens and books which have been presented to the Society since the last Anniversary; and it may not, perhaps, be here out of place to express a hope that, as we have now the means of placing and arranging books and specimens, their numbers will augment with the opportunity of placing them in safe and convenient situations.

The presents received are:

1. "A Phial containing a Curious Film of Gun Cotton, which had been formed in the interior by the Spontaneous Evaporation of the Ether from a Collodion Solution:" presented by George Phillips.
2. "The Pharmaceutical Journal:" from the Editor.
3. "The Journal of the Franklin Institute:" from the Institute.

4. "The Address delivered at the Anniversary Meeting of the Geological Society;" by Sir H. T. de la Beche: from the Author.

5. "Report of the Smithsonian Institution, and Smithsonian Contributions to Science, Vol. I.:" from the Institution.

6. "Contributions to the Science of Agriculture;" by J. T. W. Johnstone: from the Author.

7. "De Saliva;" by Nicholaus Jacuboowitsch, and "Die Diagnostik verdächtiger Flecke in Criminalfällen;" by Karl Schmidt: from Dr. Schmidt.

8. "On the Motion of Gases, Part II.;" by Thomas Graham: from the Author.

9. "Proceedings of the Royal Society of Edinburgh, No. 33 and 34:" from the Society.

10. "On the Use of the Blowpipe;" by Professor Plattner; translated by S. Muspratt: from the Translator.

11. "Taylor's Calendar of the Meetings of Scientific Bodies:" from the Author.

12. "The New and Admirable Arte of Setting of Corne, 1601," being a reprint: from H. Nesbitt.

13. "On the Composition and Money-value of different varieties of Guano;" by J. T. Way: from the Author.

14. "Transactions of the Royal Academy of Stockholm;" "An Introductory Lecture on the Importance of Chemistry;" "Annual Report of the Progress of Science;" by Dr. Svanberg: from the Royal Academy of Sciences at Stockholm.

15. "On the Nitro-prussides;" by Dr. Playfair: from the Author.

16. "Proceedings of the Philosophical Society of Glasgow, Vol. III, No. 1:" from the Society.

17. "Experimental Investigation of the Amount of Water given off by Plants during their Growth," by J. B. Lawes; and "Agricultural Chemistry," by the same: presented by J. H. Gilbert.

18. "Address Delivered at the Anniversary Meeting of the Geological Society of London, on the 16th of February, 1849;" by Sir H. T. de la Beche: from the Author.

19. "On Benzole;" by C. B. Mansfield: from the Author.

20. "Transactions of the Royal Society for 1848-9;" from the Royal Society.

21. "Regnault's *Traité de Chimie*:" from the Author.

22. "Miscellaneous Results for the Laboratory, and on the Properties of Linseed Oil Cake;" by J. T. Way: from the Author.

23. "The Quarterly Journal of the Geological Society:" presented by the Society.

The following Gentlemen were elected Officers and Council for the ensuing year :

## PRESIDENT.

Richard Phillips, F.R.S.

## VICE-PRESIDENTS.

W. T. Brande, F.R.S.	W. A. Miller, M.D., F.R.S.
Thomas Graham, F.R.S.	Lyon Playfair, F.R.S.

## SECRETARIES.

B. C. Brodie, F.R.S.	Robert Warington, Esq.
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## FOREIGN SECRETARY.

A. W. Hofmann, Ph.D.

## TREASURER.

Robert Porrett, F.R.S.

## COUNCIL.

Thomas Andrews, M.D.	J. P. Joule, Esq.
John Blyth, M.D.	G. D. Longstaff, M.D.
William Ferguson, Esq.	Theophilus Redwood, Esq.
Edward Frankland, Ph.D.	Edward Schunck, Esq.
J. J. Griffin, Esq.	E. F. Teschemacher, Esq.
H. B. Jones, M.D.	A. W. Williamson, Ph.D.

The Secretary read a list of the Contributions towards the expenses of the Charter, when Professor Graham proposed, and Dr. Longstaff seconded, a vote of thanks to the Contributors.

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The following audited Report of the Treasurer was submitted to the Society :



# AUDITED REPORT OF THE TREASURER.

Dr. ROBERT PORRETT (TREASURER) IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON. Cr.

Dr.		£.	s.	d.	1850.		£.	s.	d.	Cr.
1849.	To Balance from old Account	67	2	4	March 25.	By Payment for a Silver Candelabrum, presented to W. Tooke, Esq., in acknowledgment of his services in obtaining the Charter	30	0	0	
1850.	" 3 Year Dividend on £400 Consols to 5th Jan. 1849	5	16	6	"	" Ditto to Dunn and Duncan for Engraving and Binding the Charter	5	5	0	
March 25.	" 1 Year Ditto on £250 Consols to 5th Jan. 1850	73	7	0	"	" Ditto for Book-binding	6	13	5	
"	" Subscriptions received for Arrears prior to 1849	301	1	0	"	" Ditto for Printing and Editing Journals 5, 6, 7, and 8	165	4	5	
"	" Ditto for the Years 1849 and 1850	4	0	0	"	" Ditto for Rent to Society of Arts	25	0	0	
"	" Composition from a resident Member	20	0	0	"	" Ditto for Printing	14	1	10	
"	" 5 Ditto from non-resident Members	50	0	0	"	" Ditto for Stationery and Postage Stamps	3	16	6	
"	" Admission Fees	22	0	0	"	" Ditto for Books and Journals	10	6	6	
"	" Donations towards Charter expenses	14	2	0	"	" Ditto for Subscription to Cavendish Society	1	1	0	
"	" Ditto towards a Library Fund	2	2	0	"	" Ditto for Tea and Coffee	8	10	9	
"	" Sale of "Memoirs," &c.	6	13	8	"	" Ditto for Servants and Doorkeeper (Society of Arts)	1	10	0	
"					"	" Ditto for Collector's Poundage	17	9	0	
"					"	" Ditto for Carpenter's Work	2	7	7	
"					"	Balance carried to new Account	282	4	2	
		£ 573	10	2			£ 573	10	2	

London, 25th March, 1850.

R. PORRETT, Treasurer to Chemical Society.

We have examined the Accounts of the Chemical Society of London, presented by Robert Porrett, Esq., the Treasurer, and find the same correct, showing a balance of £282 4s. 2d., and £250 Three per cent. Consols, in his name as Treasurer, £238 14s. 5d. being in the hands of Messrs. Coutts and Co., and £43 3s. 9d. in the hands of the Treasurer.

WARREN DE LA RUE,  
DUGALD CAMPBELL,  
EDWARD J. CHEFRAX, } AUDITORS.

April 1, 1850.

THOMAS GRAHAM, Esq., V.P., in the Chair.

The following presents were announced :

"The Pharmaceutical Journal for March : " from the Editor.

"Outlines of Qualitative Analysis for Laboratory Practice," by J. Muspratt: from the Author.

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April 15, 1850.

THE PRESIDENT (Richard Phillips, Esq.) in the Chair.

Joseph Danson, Esq., Edward S. Tudor, Esq., and Alfred Anderson, Esq., were elected Fellows of the Society.

The following presents were announced :

"Journal of the Franklin Institute : " from the Institute.

"On the Diffusion of Liquids," by Professor Graham: from the Author.

The following papers were read :

XIII.—*On the Relations between the Chemical Composition and the Boiling Points and Specific Volumes.*

By PROFESSOR HERMANN KOPP.

I had formerly established the fact that, with analogous compounds, a difference of  $C_2 H_2$  in their composition, corresponded to a constant difference of about  $19^0$  in their boiling points, and likewise to a constant difference in their specific volumes. I determined the latter finally\* to be about  $21.8$ , for the boiling points of the substances in question ; *e.g.* the specific volume of alcohol being  $58.5$ , that of methyl-alcohol was found to be  $38.6$ , difference  $19.9$ .—Dr. Miller† has since made use of Pierre's observations to put these statements to the test, and believes himself warranted in concluding that they are contradictory to facts, because the numbers obtained by Pierre's observations, which, according to the above statements,

\* Ann. Ch. Pharm. L, 71.

† Chem. Soc. Qu. J. I, 363.

should be constant, are found in reality to exhibit too many discrepancies. I cannot believe this conclusion to be correct. The results of Pierre have been contradicted in part, and, I believe corrected by some researches conducted by myself with the greatest possible care.\* The following table shows a comparison of the numbers arrived at by the observations of Pierre and myself, for the boiling points and specific volumes :

	The difference for the boiling points.		$C_2H_2$ in the specific volume.	
	Pierre.	Kopp.	Pierre.	Kopp.
Alcohol and methyl-alcohol . . . . .	12 <sup>0</sup> ·0	12 <sup>0</sup> ·9	19·3	19·9
Iodide of ethyl and iodide of methyl . . . . .	26·2	—	17·5	—
Bromide of ethyl and bromide of methyl . . . . .	27·7	—	20·0	—
Acetate of oxide of ethyl and acetate of oxide of methyl . . . . .	15·6	18·0	14·7	23·6
Butyrate of oxide of ethyl and butyrate of oxide of methyl . . . . .	16·9	18·9	36·9	23·5
Acetate of oxide of ethyl and formiate of oxide of ethyl . . . . .	21·2	19·4	20·0	22·7
Acetate of oxide of ethyl and butyrate of oxide of methyl . . . . .	27·9	21·6	7·0	18·8
Butyrate of oxide of ethyl and acetate of oxide of ethyl . . . . .	17·4	20·2	13·5	21·1
Butyrate of oxide of methyl and acetate of oxide of methyl . . . . .	21·3	19·8	10·4	21·2
Butyrate of oxide of methyl and formiate of oxide of ethyl . . . . .	24·6	20·5	13·1	20·8
Butyrate of oxide of ethyl and formiate of oxide of ethyl . . . . .	22·0	20·0	21·0	21·7
Butyrate of oxide of ethyl and acetate of oxide of methyl . . . . .	19·8	19·5	19·3	22·0
Hydrated oxide of amyl and alcohol . . . . .	17·8	17·6	20·3	20·3
Hydrated oxide of amyl and methyl-alcohol . . . . .	16·3	16·4	20·1	30·2

It will be seen from the above, that many of the numbers which were found by Pierre's researches, and exhibit the greatest discrepancies from my statements, are very different from those arrived at by my determinations, which agree very nearly with the laws. The existence of a kind of law cannot be denied, even if the numbers, which should be constant, are found by experiment to exhibit discrepancies.

\* Pogg. Ann. LXXII, 223.

XIV.—*On the Preparation of certain Chlorates, particularly of Chlorate of Potash.*

By F. CRACE-CALVERT, F.C.S., *Professor of Chemistry to the Royal Institution, Manchester.*

Owing to the importance which chlorate of potash has acquired within the last two or three years in our manufacturing districts, due principally to its application as an oxidizing agent in steam colours, to raise their intensity and increase their beauty, and also in consequence of the high price, which commercial potashes have attained during the last two years, without any prospect of becoming cheaper, I was induced a few months back to try if any other chlorate could be introduced as a substitute for that of potash; and also whether a cheaper method could not be devised for manufacturing that important commercial product, of which the useful application as an oxidizing agent is greatly impeded by its high price. For it is well known that potashes have averaged for the last two years from £2 to £2. 5s. a hundred weight, which quantity does not contain above 39 to 41 per cent of potash, the remaining amount of alkali often quoted to exist in the salts being soda. It may be stated that in all the potashes which I have analysed, I have uniformly found from 10 to 12 per cent of soda.

My attention was first directed to the preparation of the chlorate of lime, which I produced by passing a current of chlorine gas into a thick milk of lime nearly boiling. It appeared, after several experiments, that heat had great influence in assisting the oxydation of the chlorine. For whilst at ordinary temperatures I could only obtain hypochlorite of lime, at about 200° or 212° F., little or no hypochlorite was formed, but a large amount of chlorate of lime.

It will be seen immediately, that it was the observation of the remarkable influence of a temperature of about 212° F., to increase the degree of acidification of chlorine, which led me to the discovery of a new method of preparing chlorate of potash.

I tried for some time to find a mode of separating chlorate of lime from chloride of calcium. But the chlorate is not to be separated with facility from the highly deliquescent chloride of calcium.

A curious chemical reaction was observed to take place several times, during the numerous trials which were made on this point. It was that large amounts of pure oxygen were often given off;

and on every recurrence of such an action, no chlorate was produced.

I next directed my attention to the preparation of the chlorate of baryta, the commercial manufacture of which would have been greatly enhanced by the recent opening of an extensive mine of carbonate of baryta at Pride Hill, in Wales, near Shrewsbury. The mineral referred to, yields on an average 90 per cent of pure carbonate: in fact its high degree of purity has caused its successful application at the potteries, and also in the finishing of calicoes, as a substitute for carbonate of lead in the glazing of cards, &c.

I at first followed the process described in chemical works, namely, the passing of a current of chlorine gas through water holding carbonate of baryta in suspension. Instead of forming chlorate, I only produced a hypochlorite; but when a heat of from 200 to 212° F. was communicated to a thick milk of carbonate of baryta, one of the neatest chemical reactions took place, for the whole mass was transformed into chlorate of baryta, and chloride of barium.

It appeared to me at the time that a cheap substitute for chlorate of potash was thus obtained. But I was deceived; as it was found impossible to separate in a satisfactory manner the chlorate of baryta from the chloride of barium, even by seven or eight consecutive crystallizations from water. Though certainly the chlorate was becoming gradually purer, still it was impossible to free that salt completely from chloride of barium. Although this coincidence in the solubility of these two salts had been remarked by Chenevix, still as in most works, the chlorate of baryta is stated to be employed to prepare chloric acid, I persevered, but regret to say in vain. I even tried to separate these two salts, by treating them with rectified spirits and wood-naptha or the hydrate of oxide of methyl, but without success.

I next directed my efforts to discover a cheaper method than those hitherto known, of preparing the chlorate of potash.

It is necessary here to mention, that the chlorate of potash is not now generally manufactured by passing chlorine into a concentrated solution of carbonate of potash, but that the useful process recommended by Professor Graham, namely of carrying a current of chlorine through a mixture of sulphate of potash and lime, has been generally adopted, and has given satisfactory results.

I placed myself in the best circumstances for ascertaining the relation of this process to the one hereafter described. One equivalent or 97 parts of sulphate of potash, dissolved in a sufficient amount of water, and mixed with six equivalents of lime, or 168

parts, was submitted to a current of chlorine, at  $212^{\circ}$  F. Although chlorate of potash was formed, in this experiment, yet its quantity was inferior to the theoretical amount, namely 122.5 parts.

From this, and other experiments, and also from information which I have obtained, I find that, commercially, 122.5 parts of chlorate of potash are never produced from 97 parts of sulphate of potash. No doubt, this result is due to the formation of a certain amount of chloride of potassium, in addition to the imperfect decomposition of the sulphate of potash by the lime.

A mixture of chloride of potassium with lime was also submitted to experiment, but yielded no satisfactory results.

It was several months after my researches were completed, that I learnt from Professor Graham himself, that he had published in the "Transactions of the Chemical Society," (Vol. I. p. 5) a short notice on the production of the chlorate of potash by means of a mixture of carbonate of potash and lime. Still this chemist has not inquired into the precise bearing of his interesting observation as to the best mode of conducting the process commercially, and the amount of chlorate produced.

I was led by a series of consecutive trials to examine what would take place by passing chlorine gas at ordinary temperatures through a solution of caustic potash containing caustic lime in suspension. Under these circumstances, I only produced the hypochlorites of potash and lime, and the chlorides of potassium and calcium; but if the chemical action was assisted by heat, chlorate of potash was formed in large amount instead of hypochlorite.

It is certainly interesting to see in this series of experiments, how a comparatively small increase of temperature (from  $60^{\circ}$  to  $180^{\circ}$ ) modifies chemical action and assists the fixation of an additional amount of oxygen by the chlorine.

Having been successful so far, my attention was next directed to the best means of producing by this method the largest amount of chlorate of potash, an object which I arrived at by examining the influence of solutions of caustic potash, more or less concentrated, upon the quantity of salt produced.

For my first experiment, a solution of caustic potash of specific gravity 1.040, at  $60^{\circ}$  F., was taken, containing 34 grains of real potash in 1000 fluid grains of liquid. In order also to act always on the same proportion of potash, a constant bulk of fluid was taken, which contained exactly 100 grains of oxide of potassium. In this case, therefore, 3000 fluid grains were made use of, containing 102 grains of potash. I then took 6 equivalents of good quick lime, or



358 grains, which after being slaked were added. The mixture being heated to about  $200^{\circ}$  F., a rapid current of chlorine was passed through, as long as the gas was absorbed. The whole was thrown on a filter, and the small deposit washed with boiling water. The liquor in cooling yielded a fair amount of chlorate, which was slightly increased by the concentration of the mother-liquor. The quantity was 130 grains of chlorate, or 3 times as much as potash alone would have given.

A second experiment was made with a solution of caustic potash of specific gravity 1.050, and containing 40 grains of potash in 1000 fluid grains; consequently 2778 grains of this caustic solution were taken, and contained 100 grains of oxide of potassium. After being mixed with the required proportion of slaked lime, they were submitted to the operation above described, and gave 140 grains of chlorate of potash, exclusive of a small amount of that salt left in the mother-liquor. As an increase in the quantity of caustic potash for a given bulk of fluid appeared, therefore, favourable, a third trial was now made with a solution of specific gravity 1.070, containing 58.75 grains of oxide of potassium in 1000 fluid grains; or 1750 grains contained 102 grains of oxide of potassium. In this trial, 158 grains of chlorate were produced.

Such details on the action of chlorine on solution of caustic potash at different strengths may be excused, as they afford an interesting illustration of the modifications which chemical actions may undergo in consequence of the influence of small changes, either in the mode of operating, or in the medium in which the reactions takes place. The results perfectly corroborate the facts which I formerly observed respecting the action of ammonia on the nitrate of lead, as well as the remarks which I then made on the formation of the salts resulting from the action of these two compounds.

It was necessary to proceed very cautiously with this series of experiments, as I had remarked that if a particular strength in the solution of caustic potash was exceeded, I then produced chloride of potassium and less chlorate. Another serious impediment was also created by the liquor becoming so thick, by the amount of lime required for a given weight of potash, that the free passage of chlorine gas was prevented.

In a fourth experiment I took a solution of caustic potash of specific gravity 1.090 at  $60^{\circ}$  F. A quantity of liquor containing 100 grains of potash gave 172 grains of chlorate.

In a fifth trial, a liquor of specific gravity 1.099 being used, 100 grains of potash gave 185 grains of chlorate, besides some left in

the mother-liquor. This last quantity already exceeded more than four times that which potash alone would have furnished.

In a sixth experiment, an enormous amount of chlorate was produced, amounting, as it will be seen, to nearly the theoretical proportion, namely 260 parts of chlorate for 100 parts of potash; and I have no doubt that in manufactures, the amount produced would be still nearer, as the portion left in the mother-liquor would be comparatively less.

A solution was finally employed of caustic potash of specific gravity 1.110, or containing 10.233 per cent of real potash; consequently the quantity of fluid operated upon, 1000 fluid grains, contained 102.33 grains of oxide of potassium. To this liquid was added 358 grains of quick lime previously slaked. The whole being slightly heated, a rapid current of chlorine gas was passed through, the temperature rising very fast to  $180^{\circ}$  F., owing to the intensity of the chemical action. The operation was considered complete when the liquid refused to absorb any more gas; the whole was then evaporated nearly to dryness, the residue dissolved in boiling water, and the liquor filtered. After washing the slight deposit left on the filter, the whole of the liquors were evaporated for crystallization. The amount of chlorate of potash obtained in this experiment was equal to 220 grains, with some salt still left in the mother-liquors. The last no doubt amounted to nearly 20 grains, owing to the rather large bulk of mother-liquors which were reserved, so as to prevent the chlorate from being soiled with chloride of potassium.

It is certainly remarkable that there should be a determinate specific gravity where the chemical reaction is brought to bear to its fullest extent, or where, in other words, the whole of the potash is transformed into chlorate, while in solutions of greater or less specific gravity, a smaller quantity of chlorate is produced with a corresponding increase of chloride of potassium. This chemical reaction is rendered still more worthy of notice by the influence of the above fact in modifying the action of chlorine, relatively to its affinity for potassium or calcium. Thus, in a liquor of specific gravity 1.110, we find that calcium takes precedence of potassium, in combining with chlorine, and preserves the latter metal almost entirely from the action of chlorine; while the oxygen, disengaged from the calcium, applies itself to the chlorine, to transform the latter into chloric acid, which neutralizes the potash only. This, so far as I am aware, is the only example which chemistry affords, where, in the presence of two bases, the chlorine applies itself almost *entirely* to one of the metals, whilst oxygen attaches itself to the chlorine, converting it

into an acid which neutralizes exclusively the second base, namely the potash.

The commercial advantages of the above process over the old one, will be easily conceived, when we reflect that, in the latter, 100 parts of oxide of potassium yielded only 43 parts of chlorate, whilst, treated by the method here recommended, 100 parts of the same oxide give nearly 260 parts of chlorate of potash.

The chlorate may be produced by the new process at about sevenpence per pound, and might therefore be supplied on terms which are greatly below the present market price.

Before concluding, I have much pleasure in acknowledging the valuable assistance which I have received in this inquiry from one of my former pupils, Mr. Charles O'Niel, of this town.

#### XV.—On "*Propylene*," a new Hydrocarbon of the series $C_n H_n$ .

By CAPTAIN JOHN W. REYNOLDS, F.C.S.

The formula  $C_n H_n$ , represents a numerous group of bodies, containing an equal number of equivalents of carbon and hydrogen, of which the well-known olefiant gas,  $C_4 H_4$ , may be taken as the type.

For many years this latter stood alone, till Mr. Faraday, in his research upon compressed oil-gas, published by the Royal Society in 1825,\* showed the existence of another substance of like percentage composition, but distinguished from it by the number of carbon and hydrogen equivalents condensed into the same space; since that time, the progress of science has made us acquainted with a numerous series of similar bodies.

The dehydration of the alcohols  $C_n H_{n+2} O_2$ , or  $C_n H_n, 2 HO$ , has been the chief, but by no means the only source of these hydrocarbons, which are also formed in several processes of destructive distillation, and in the metamorphoses of various compounds connected with the alcohols.

The consequence of this diversity of origin, and the propriety of each alcohol to give rise, in addition to a hydrocarbon containing the same number of carbon equivalents as itself, to several metameric bodies, is that the series  $C_n H_n$  exceeds in number that of the alcohols  $C_n H_{n+2} O_2$ , though it does not reach to that of the acids  $C_n H_n O_4$ , with which both are associated.

\* Phil. Trans. 1825.

The result of the experiments detailed in the following pages, has been to supply a term hitherto wanting in the series, the position of which will be best understood by inspection of the subjoined table, in which all the members of the series  $C_n H_n$ , at present known, are given, together with the corresponding alcohols, so far as we are acquainted with them.

Methyl-alcohol . . .	$C_2 H_4 O_2$	Methylene . . .	$C_2 H_2$
Ethyl-alcohol . . .	$C_4 H_6 O_2$	{ Ethylene . . . Ethene . . . Olefiant gas . . }	$C_4 H_4$
" "	"	" "	"
" "	"	{ Butylene . . . Ditetryl . . . }	$C_8 H_8$
Amyl-alcohol . . .	$C_{10} H_{12} O_2$	Amylene . . .	$C_{10} H_{10}$
" "	"	{ Caproylene . . . Olène . . . }	$C_{12} H_{12}$
" "	"	" "	"
" "	"	{ Naphthylene . . . Naphthene . . . }	$C_{16} H_{16}$
" "	"	Paramylene . . .	$C_{20} H_{20}$
" "	"	" "	"
Cetyl-alcohol . . .	$C_{32} H_{34} O_2$	{ Cetylene . . . Cetene . . . }	$C_{32} H_{32}$
" "	"	" "	"
" "	"	Metamylene . . .	$C_{40} H_{40}$
" "	"	" "	"
C'erotyl-alcohol . . .	$C_{54} H_{56} O_2$	{ Cerotylene . . . Cerotene . . . }	$H_{54} H_{54}$
C'erotin . . .	"	" "	"
" "	"	" "	"
Melissyl-alcohol . . .	$C_{60} H_{62} O_2$	{ Melissylene . . . Melene . . . }	$C_{60} H_{60}$
Melissin . . .	"	" "	"

In this table are not included a number of isomeric hydrocarbons, said to be contained in coal-tar naptha, and present in the various kinds of petroleum, and also obtained by the distillation of the fatty acids, because their position on the scale has not been sufficiently well established; even the table contains some terms concerning which doubts still exist.

Methylene\* has been obtained only once by Dumas and Peligot, and, as appears from their account, not in a state of absolute purity.

\* Ann. Ch. Phys. [2] LVIII, 1.

Ethylene, ethene, or olefiant gas, is obtained, as is well known, by the de-hydration of ordinary alcohol.

The alcohol corresponding to the next term in the table  $C_8 H_8$ , is not known, but the hydrocarbon itself was obtained originally by Faraday,\* as before mentioned, from the liquid condensed from oil-gas; the same body, according to Bouchardat,† appears to exist among the products of the dry distillation of caoutchouc; and Kolbe‡ has also lately obtained it, as a product of the decomposition of valeric acid by the battery.

Amylene has been studied by Balard,§ who obtained it by the action of chloride of zinc upon amyl-alcohol or fusel-oil.|| The reaction with chloride of zinc gives rise also to the formation of paramylene, originally obtained by Cahours,¶ in the corresponding process with phosphoric acid, and metamylenes, whose formulæ have been controlled by the determination of the density of their vapours.

Caproylene is one of the hydrocarbons obtained by Fremy,\*\* in the destrusive distillation of several fatty acids; it was originally described under the name oleene.

Among the various hydrocarbons, separated from naphtha, by Pelletier and Walter,†† one has been studied with particular attention. This substance, called by the discoverers naphthene, is very probably the term  $C_{16} H_{16}$ .

Cetylene is the hydrocarbon of the cetyl-alcohol, discovered by Dumas and Peligot,‡‡ in their researches on spermaceti.

Cerotylene and melissylene, are derived from the interesting wax-alcohols discovered by Mr. Brodie.§§ The formulæ in the

\* Phil. Trans. 1825.

† J. Pharm. XXIII, 454.

‡ Chem. Soc. Qu. J. II, 157.

§ Ann. Ch. Phys. [3] XII, 294.

|| The same body is formed, together with various substances, in the decomposition of iodide of amyl by zinc; for on comparing the composition and properties of the compound lately described by Frankland (Chem. Soc. Qu. J. III. 30), under the name of valerene, there cannot be the slightest doubt that it is nothing but Balard's amylene. Both substances contain the same amount of carbon and hydrogen, and exhibit the same state of condensation. Their physical properties are absolutely identical; and if Mr. Frankland has observed a boiling-point a few degrees lower than Balard, this is perfectly intelligible on the supposition that his substance still contained traces of the more volatile hydride of amyl. Valerene was observed to boil at  $35^{\circ}$ ; the boiling-point of Balard's amylene is  $39^{\circ}$ , which has lately been verified by Mr. Medlock, who has prepared this body on a large scale.

¶ Ann. Ch. Phys. [2] LXX, 81.

\*\* Ann. Ch. Pharm. XX, 50.

†† Compt. Rend. IX, 146.

‡‡ Ann. Ch. Phys. [2] LXII, 1.

§§ Phil. Trans. 1849.

table are the same as those given by Mr. Brodie, although there is still some doubt as to whether they are actually the correct ones; the doubt arising from the fact of the substances in question being metamorphosed by the action of heat, and consequently not admitting of density-determinations.

The first term missing (the alcohol of which is likewise unknown) in the above series, is that which should occupy the place between olefiant gas and butylene.

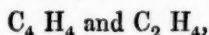
It is this hydrocarbon, whose composition must be represented by the formula



that the succeeding experiments have supplied, and to which I propose to give the name of *Propylene*. This name is, like those of the rest of the series derived from the corresponding alcohol, in this case still unknown, and for which the appellation of Propylic alcohol has been suggested by Dr. Hofmann.

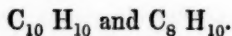
#### PREPARATION OF PROPYLENE.

It is well known that the vapour of alcohol is entirely decomposed on passing through a red-hot tube, and that the products of decomposition are principally olefiant gas and marsh gas,



together with several fluid, and even solid bodies, which have not yet been more closely investigated.

Amyl-alcohol, or fusel-oil, under similar treatment, might have been expected to yield analogous results in the production of the bodies,



It was the investigation of this point that gave rise to the discovery of the hydrocarbon  $\text{C}_6 \text{H}_6$ , which is the object of the present communication.

The arrangement employed was as follows:

A long tube of hard German glass was placed in a combustion-furnace, one end being connected with a flask containing fusel-oil, and the other, after passing through a Liebig's condenser, bent so as to dip into a Woulfe's bottle partly filled with water, which latter was furnished with a flexible tube to convey the evolved gas into a gasometer.

When the tube was red-hot, the fusel-oil in the flask was made to boil briskly, which caused an abundant evolution of gas, and a quantity of



liquid collected in the Woulfe's bottle, which appeared to consist of undecomposed fusel-oil, though it is possible further examination might show that liquid products of decomposition are also present.

The quantity and quality of the gas evolved were greatly influenced by the temperature of the tube. When the heat was too great, little besides ordinary marsh gas was obtained; on this account, an iron tube could not be employed. If, on the other hand, the temperature was not sufficiently high, the greater portion of the fusel-oil passed over undecomposed, and but little gas could be collected.

When the operation was properly conducted, the resulting gas burnt with a highly luminous flame, and when brought into contact with chlorine or bromine, gave rise to an abundant formation of oily drops, in a manner similar to that of olefiant gas.

Some preliminary experiments showed that the gaseous product thus obtained was a mixture of different substances, the proportions of which appeared to vary considerably, even in operations which were considered successful; hence there appeared but little chance of obtaining satisfactory results from eudiometrical analysis; I, therefore, decided to submit to closer examination the product obtained by the action of bromine upon the crude gas, by which alone a considerable separation was effected.

#### BROMINE-COMPOUND.

This compound was formed in the following manner: The gas was collected in bottles, and bromine added in small portions, the bottles being shaken at the same time till the bromine ceased to be decolorized. In this manner a quantity of a heavy oily liquid was obtained, which was washed with water, dried over chloride of calcium, and subsequently purified by repeated distillations off quick lime. It is not advisable to prepare this compound by passing the gas directly into bromine, as experiment showed that, under these circumstances, a large quantity of substitution-bodies was formed, diminishing considerably the amount of the chief product of the reaction.

The limpid oil obtained as above described began to boil at  $136^{\circ}$  C., the boiling-point rising rapidly to  $143^{\circ}$ , where it remained stationary for a considerable time, and subsequently rose slowly to  $160^{\circ}$ , when a quantity of a brown liquid remained in the retort, which at that temperature began to decompose, with evolution of hydrobromic acid; a portion, more than three-fourths of the

whole, was ultimately separated by repeated distillation; its properties are as follow :

It is a colourless oil, of an ethereal odour, slightly alliaceous, and very similar to that of Dutch liquid. Its boiling-point is  $143^{\circ}$  C. It does not solidify at  $-20^{\circ}$  C. Its specific gravity is 1.7. It is decomposed by concentrated sulphuric acid.

Combustion with chromate of lead and oxidized copper-turnings gave the following results :

- I. 0.5709 grm. of substance gave :  
 0.3839 " " carbonic acid, and  
 0.1526 " " water.  
 II. 0.4811 " " substance gave :  
 0.3170 " " carbonic acid, and  
 0.1346 " " water.  
 III. 0.6305 " " substance gave :  
 0.4095 " " carbonic acid, and  
 0.1729 " " water.

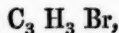
The bromine was determined by combustion with lime in the usual manner :

- IV. 0.7934 grm. of substance gave :  
 1.4974 " " bromide of silver.  
 V. 0.5115 " " substance gave :  
 0.9640 " " bromide of silver.

Percentage-composition :

	I.	II.	III.	IV.	V.
Carbon . .	18.33	17.97	17.71	—	—
Hydrogen .	2.96	3.10	3.04	—	—
Bromine .	—	—	—	78.58	79.07

The simplest expression to which these numbers lead is the formula :



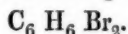
as may be seen from the following comparison of the theoretical and experimental values :

	Theory.		Mean of Experiment.
3 equivs. Carbon . . .	18.00	18.13	18.00
3 " Hydrogen . . .	3.00	3.02	3.04
1 equiv. Bromine . . .	78.26	78.85	78.83
	<hr/> 99.26	<hr/> 100.00	<hr/> 99.87

The determination of the density of the vapour, however, proves that this formula must be doubled, if we admit that the elements are condensed in a manner similar to that which obtains in the corresponding member of the olefiant gas series.

Weight of flask with dry air . . .	33.2504	grms.
Temperature of balance case . . .	22.25°	C.
Height of barometer . . .	759.4	mm.
Temperature at time of sealing . . .	198°	C.
Weight of flask with vapour . . .	34.0879	grms.
Height of barometer . . .	759.0	mm.
Volume of air remaining in the flask . . .	4.0	cc.
Volume of mercury filling flask . . .	204.5	cc.

The density of the vapour deduced from the above data is 7.3098, which, on comparison with the following theoretical value, will show that the formula of the compound in question must be:



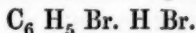
6 equivs. Carbon	= 6 vols. =	4.9920
6 „ Hydrogen	= 12 vols. =	.8316
2 „ Bromine	= 4 vols. =	22.1776
		<hr/>
		28.0012

On dividing this total by 4, we have:

	Theory.	Experiment.
$\frac{28.0012}{4}$	= 7.0003	7.3098

The excess above the theory is probably due to the partial decomposition of the vapour, which caused a small quantity of carbon to be deposited in the flask.

If we adopt for the analogous body in the olefiant gas series, the term hydrobromate of bromide of acetyl, we may call the present compound, hydrobromate of bromide of propionyl,



On digesting the oil just described with alcoholic solution of potash, very energetic action took place, with abundant deposition of bromide of potassium, and a liquid distilled over, from which, on the addition of water, a heavy, colourless, and very mobile fluid separated, extremely volatile, and of a peculiar odour, resembling that of rancid fish.

This substance was dried over chloride of calcium, and rectified by

distillation off quick lime. Its boiling-point not being stationary, it was treated several times with alcoholic solution of potash, which, however, only appeared to increase the variableness of the temperature of ebullition.

The product was therefore separated by fractional distillation into portions boiling between  $45^{\circ}$  and  $56^{\circ}$ ,  $56^{\circ}$  and  $60^{\circ}$ , and  $60^{\circ}$  and  $70^{\circ}$ .

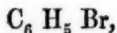
Analyses of these distillates gave the following results :

- I. 0.6495 grm. of substance boiling from  $45^{\circ}$  to  $56^{\circ}$  gave :
  - 0.6893 " " carbonic acid, and
  - 0.2348 " " water.
- II. 0.4207 " " substance boiling from  $56^{\circ}$  to  $60^{\circ}$  gave :
  - 0.4516 " " carbonic acid, and
  - 0.1580 " " water.
- III. 0.4543 " " substance boiling from  $60^{\circ}$  to  $70^{\circ}$  gave :
  - 0.5134 " " carbonic acid, and
  - 0.1891 " " water.

Percentage-composition :

	I.	II.	III.
Carbon . .	29.06	29.26	30.88
Hydrogen . .	4.03	4.17	4.62

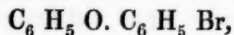
The first of these results will be seen to approximate closely to the formula



as may be seen from the following comparison :

	Theory.		Experiment.
6 equivs. Carbon . . .	36	30.18	29.06
5 " Hydrogen . . .	5	4.19	4.03
1 equiv. Bromine . . .	78.26	65.62	—
	<hr/> 119.26	<hr/> 99.99	

As the boiling-point rises, the proportion of carbon and hydrogen increases, thereby leading to the conclusion that the action of the potash produces in the first instance the body  $\text{C}_6 \text{H}_5 \text{Br}$ , and that afterwards a substance containing more or less oxygen in the place of bromine is formed. The formula of this second body may probably be



or oxybromide of propionyl, which would contain :

Carbon . . . .	42.78
Hydrogen . . . .	5.94

The great loss caused by repeated distillation, in the hope of obtaining a constant boiling-point, previous to the above hypothesis suggesting itself, left me so little substance that I was unable to determine this point more accurately.

## CHLORINE-COMPOUND.

This compound was formed by allowing the crude gas obtained from fusel-oil to meet chlorine in a quilled glass globe, when combination took place, with evolution of heat; and a heavy oily liquid, similar to the bromine-compound collected in the receiver. This liquid was dried over chloride of calcium and distilled repeatedly off quick lime, and finally a portion was obtained which boiled at  $100^{\circ}$  and  $103^{\circ}$ .

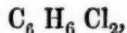
Two chlorine-determinations\* gave the following numbers:

I.	0.4618	gram. of substance gave:
	1.1694	„ „ chloride of silver.
II.	0.3659	„ „ substance gave:
	0.9256	„ „

Percentage:

	I.	II.
Chlorine . . . .	62.64	62.55

which agrees with the formula



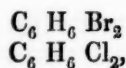
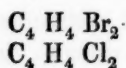
as may be seen from the following comparison:

	Theory.		Mean of Experiment.
6 equivs. Carbon . .	36.0	31.85	—
6 „ Hydrogen . .	6.0	5.30	—
2 „ Chlorine . .	35.5	62.83	62.59
	<hr/> 77.5	<hr/> 99.98	<hr/>

On treating this compound with alcoholic solution of potash, a decomposition, similar to that which took place in the case of the bromine-product, appeared to result.

The perfect analogy in composition and deportment of the compounds described, with the corresponding terms of the olefiant gas series,

\* The fraction boiling at a constant point was much smaller than in the case of the bromine-compound, a larger quantity of substitution-products being formed.

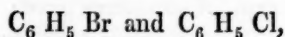


appear to warrant the conclusion that the substance which combines in the present cases with bromine, or chlorine, is the hydrocarbon

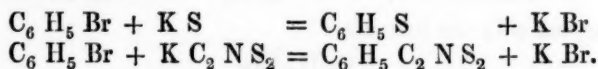


In successful operations, the proportion of propylene in the gas derived from fusel-oil, was about half the original gas. The residue, obtained by passing the gas through bromine till the latter ceased to absorb it, appeared to consist chiefly of marsh gas; but this point demands a more particular investigation, which I intend shortly to make. I also propose to try whether by the use of solvents, such as benzol, or oil of turpentine, it may be practicable to obtain the hydrocarbon  $\text{C}_6 \text{H}_6$  pure, so as to examine it eudiometrically.

On considering the composition of the bodies,



it will be seen that they may be regarded as belonging to the allyl-series; and it may, therefore, be anticipated that the action upon either of sulphide of potassium and sulphocyanide of potassium, will produce respectively oil of garlic, and mustard oil, sulphide, and sulphocyanide of allyl:



I intend to make these reactions the subject of further investigation, as well as to complete what is deficient in the experiments already detailed, and I hope to have the honour of submitting the results to the Society.

I may mention, in conclusion, that the above inquiry was conducted in the Laboratory of the Royal College of Chemistry, and I take this opportunity of expressing my thanks to Dr. Hofmann for his kind assistance and advice in the performance of these experiments.



XVI.—*Note upon the Action of Heat upon Valeric Acid; with some remarks upon the formulæ of the Alcohol-Radicals.*

By A. W. HOFMANN, Ph.D., F.C.S.

The interesting experiments which Capt. Reynolds has just now communicated to the Society, have pointed out the existence of a gas long anticipated by theory, but which had hitherto escaped observation. This body will most likely be found a very frequent product of the dry distillation of substances rich in hydrogen. The gases hitherto obtained in various reactions of this kind, and considered as olefiant gas, may possibly have contained, together with the latter, some proportions of this hydrocarbon  $C_6 H_6$ , and it is by no means improbable that the luminiferous properties of common coal gas, far from entirely arising from olefiant gas, may be partly due to the presence of propylene, of butylene, and even of amylene. The method used by Capt. Reynolds, in treating his gas with bromine, might be followed with advantage in order to settle this point.

By adopting this plan, I have been able to trace the evolution of propylene in a reaction which has lately engaged my attention. The vapour of valeric (valerianic) acid, when passed through a red-hot tube, yields a considerable volume of gas, together with a quantity of liquid products, the amount of which varies with the temperature at which the action is performed. Without entering into details respecting the liquid products, it may at once be stated that the gas consists chiefly of hydrocarbons of the formula  $C_n H_n$ , together with the oxides of carbon. After having removed the carbonic acid by means of an alkali, these hydrocarbons were absorbed by bromine-vapour; the residuary gas then burned with a blue flame, and was found to consist of carbonic oxide. On passing it into pentachloride of antimony, it was at once converted into phosgene gas, readily recognized by its nauseous odour, and by disappearing when conducted into water, with formation of carbonic and hydrochloric acids. In several operations, the gas, after having passed successively through potassa, bromine, pentachloride of antimony, and water, was no longer inflammable, consisting now of accidental atmospheric air; in others, a mere trace of inflammable gas was left, which may have been a member of the marsh-gas family—most likely marsh gas itself; in contact with chlorine it yielded oily drops, doubtless of chloride of carbon.

On submitting the oily fluid, obtained in the absorption of the

series  $C_n H_n$ , to ebullition, the thermometer rose at once to  $130^{\circ} C$ . The main bulk of the liquid passed over between  $136^{\circ}$  and  $156^{\circ}$ , when hydrobromic acid was evolved, arising from the decomposition of the small quantity of substitution-products, the formation of which can never be altogether avoided. On redistilling the resulting liquid, the thermometer became tolerably stationary between  $143^{\circ}$  and  $145^{\circ}$ , when about half of the compound passed over.

As I was unable to subject the product, which had been prepared on a small scale only, to an elaborate purification, I could expect from analysis but approximate results.

- I. 0.4696 grm. of oil gave :  
 0.3245 " " carbonic acid, and  
 0.1350 " " water.  
 II. 0.2805 " " oil gave :  
 0.5276 " " bromide of silver.

These numbers lead to the following percentage :

Carbon . . . . .	18.84
Hydrogen . . . . .	3.19
Bromine . . . . .	80.00

These numbers, although evidently incorrect, nevertheless so closely approach the percentage of Capt. Reynolds' hydrobromide of bromide of propionyl, that I do not hesitate to assume that the bromine-compound examined actually consisted chiefly of this substance, contaminated most likely with a small quantity of a substitution-product, and possibly of the corresponding terms in the ethylene- and butylene-series. For the sake of comparison, I adduce the percentage of these several substances :

	$C_4 H_4 Br_2$	$C_6 H_6 Br_2$	$C_8 H_8 Br_2$
Carbon . . .	12.77	17.82	22.22
Hydrogen . .	2.12	2.97	3.70
Bromine . . .	85.11	79.21	74.08
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Of the oil distilling at a lower temperature, I have only made a bromine-determination.

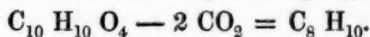
- 0.3237 grm. of oil gave :  
 0.6455 " " bromide of silver.

Percentage of bromine 84.83.

This number, as well as the boiling-point, sufficiently showed that this substance consists chiefly of the bromine-compounds of olefiant gas.

The chief bulk then of the hydrocarbons evolved in the decomposition of valeric acid by heat, would appear to consist of propylene, accompanied by small quantities of olefiant gas and possibly of butylene. I could not, however, affirm the presence of the latter. The experiments of Capt. Reynolds, on the action of heat on amyl-alcohol, were made on a sufficiently large scale to prove that in this reaction, in addition to propylene, no other term of the same series is formed in considerable quantity. I was unable to devote so large a quantity of valeric acid to the attainment of an equal degree of precision, and therefore leave it doubtful whether butylene is actually formed in this reaction.

The results obtained in the dry distillation of valeric acid, were far from what I had anticipated when I undertook the experiment. I had hoped to see this acid imitate the deportment of acetic or benzoic acid under similar circumstances; these acids being converted, with the loss of 2 equivs. of carbonic acid, the one into marsh gas, the other into benzol. A similar behaviour of valeric acid would have given rise to the formation of a compound  $C_8 H_{10}$ ,



The experiments which I have just now detailed, show that the compound in question is not found among the gaseous products of the decomposition of valeric acid. It appears that this term,\* unable to exist at the prevailing temperature, is broken up into the more stable compounds of the series  $C_n H_n$ , the excess of hydrogen being eliminated either in the form of marsh gas, or as water, formed by the reduction of carbonic acid to carbonic oxide. Several experiments, in which the temperature was so far lowered as to allow a considerable quantity of valeric acid to distil undecomposed, yielded sensibly the same results; nor was much difference observed when the tubes were filled with pumice-stone, or when, in order to fix the carbonic acid, valeric acid was distilled with an excess of baryta. In the latter experiment, together with the hydrocarbons  $C_n H_n$ , pure hydrogen gas appeared to be evolved.

\* The members of this series appear to be far less stable than the hydrocarbons containing an equal number of carbon- and hydrogen-equivalents. The rapid distillation of margaric acid with and without lime, appears to yield hydrocarbons of the family  $C_n H_n$  only; this subject, however, is by no means sufficiently examined. The instability of these substances would also explain why we have not hitherto obtained a member of the marsh-gas-series, derived from the fatty acids in the various tars and naphthas which have been examined, whilst the more stable corresponding terms derived by loss of carbonic acid from the acids of the benzoic series, viz., benzol, toluol, xylol, cumol, cymol, have been found to be present in considerable quantities in coal-oil (Mansfield), and in the oil precipitated from wood-spirit on addition of water (Cahours).

It would be interesting to repeat the same experiment with butyric acid and propionic acid; it is possible that the greater simplicity in the construction of the terms  $C_6 H_8$  and  $C_4 H_6$ , will protect them from being broken up into inferior groups.

The preparation, under the above circumstances, of the marsh-gas term of valeric acid, acceptable as a contribution towards the completion of this hitherto apparently scanty family, would have commanded additional attention by the decision which it appeared to promise, of a very important question which is pending at this moment.

Chemists have read with unusual interest the highly remarkable researches, published within the last two years in the Journal of this Society, by Drs. Kolbe and Frankland. Dr. Kolbe, in his admirable investigation of the products formed in the electrolysis of valeric acid, first pointed out the production of a hydrocarbon, represented by the formula  $C_8 H_9$ , for which, from theoretical views peculiar to himself, he proposed the name *Valyl*. The above formula represents the radical of the missing alcohol of butyric acid. Kolbe leaves it undecided whether this body actually is the radical in question, but remarks that its vapour-density exactly coincides with this assumption.

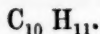
The next step was the isolation of the radical of a known alcohol, of methyl. In treating cyanide of ethyl with potassium, Drs. Kolbe and Frankland obtained, together with a beautifully crystalline alkaloid cyanathine, isomeric with the mother-compound, a permanent gas which exhibited exactly the composition and the condensation of the hypothetical radical methyl,



The mine being once opened, discoveries followed each other with rapidity. Dr. Frankland, in pursuing by himself this line of inquiry, arrived, by acting with zinc upon the alcohol-iodides successively, at the isolation of ethyl,



and lastly of amyl,



The details of these beautiful researches, performed with remarkable experimental skill, are yet fresh in the recollection of the Society.

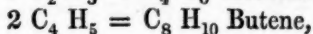
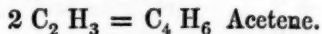
An unusual interest is attached to these investigations; the isolation of the radicals presenting in their compounds so great an

analogy to hydrogen, and replacing this element, when in a state of mobility, both in acids and bases,—the isolation of these elementary groups appeared to be the key-stone of the theoretical edifice, in the construction and elaboration of which the finest discoveries of the last twenty years had been made.

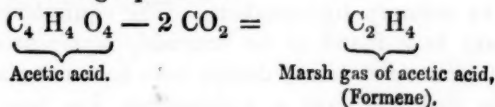
But notwithstanding the deep interest excited by these discoveries, all chemists were not perfectly satisfied with the general character exhibited by the new radicals.

Nobody expected that ethyl, like zinc, would disengage hydrogen from sulphuric acid and water, or that, like iron, it would precipitate copper or antimony. There were, however, many who thought, whether rightly or wrongly, that these substances would, under certain circumstances, like hydrogen, combine directly with chlorine; that they would combine with other elements, without giving rise to phenomena of substitution; and reproduce, like other of the isolated radicals, as cyanogen or cacodyl, some terms of their own series. The great difficulty with which free hydrogen combines with chlorine, and the powerful affinity exhibited by the latter element for hydrogen when in the combined state, militates, it is true, to a certain extent against this assumption; but we have, on the other hand, in olefiant gas and its congeners, well known instances in which this direct combination actually appears to take place. Up to this present moment, none of the supposed alcohol-radicals have been observed to combine, like cyanogen or cacodyl, directly with any of the elements; none of them have been found capable of reproducing a methyl-, ethyl- and amyl-compound.

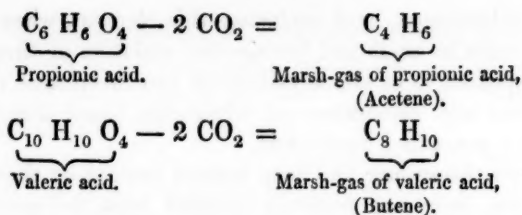
The first doubts respecting the interpretation of the experiments in question were raised by some of the French chemists. MM. Laurent and Gerhardt,\* in reporting upon the investigation of Dr. Frankland, have pointed out that the bodies described under the names of methyl and ethyl might, with more probability, be considered as homologues of marsh gas. In fact, if we double the formulæ of the substances in question :



we arrive at a series of substances, the analogy of which becomes evident by the following equations :

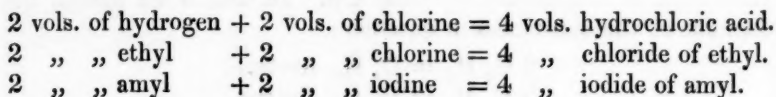


\* Compt. Rend. Trav. Chim. 1850.



The experiments upon the action of heat on valeric acid which I have communicated to the Society, had been undertaken chiefly in order to decide between the two views. If this reaction had given rise to the formation to the body hitherto called ethyl, or of a substance having the same composition, but endowed with different properties, we should have been enabled to adopt either the one or the other of these views. Unfortunately, this experiment has led to results reconcileable with both opinions, the reaction evidently going too far, and inferior terms of the family  $\text{C}_n \text{H}_n$  being produced. Unable then as I have been to bring forward any experimental evidence of my own in favour of either view, I must limit myself to adducing a few considerations in order to raise a discussion of this very important subject, which will not decide the question pending, but may lead to new experiments, and contribute to a more perfect understanding of what is meant by the often somewhat loosely employed term, organic radical.

If we assume the existence of compound radicals, which, by their juxtaposition to chlorine, bromine and iodine, give rise to the formation of the chlorides, &c., of methyl, ethyl and amyl, we are compelled to represent their molecules by 2 volumes of vapour. In this manner the constitution of the vapours of these compounds becomes perfectly analogous to that of hydrochloric, hydrobromic and hydriodic acids, in fact, of the compounds of these elements in which the radical is replaced by hydrogen:



The condensation of the vapour of the radical hydrocarbons, represented as it is by 2 volumes of vapour, is very different from that exhibited by ordinary hydrocarbons. The equivalents of these substances have been found to be invariably represented by 4 volumes of vapour. In some cases, doubts have been entertained; but it is remarkable that whenever a hydrocarbon has been well studied, especially by a careful examination of its metamorphoses, the equiva-



lent has been found to correspond to the condensation which I have mentioned. The only hydrocarbon, mesitolol, the vapour of which appeared to have a different constitution, has ceased to form an exception, since M. Cahours' careful density-determination, lately communicated to the Society.\*

The peculiar mode of condensation which we have to assume for the substances called methyl, ethyl and amyl, if we consider them as the radicals  $C_2H_3$ ,  $C_4H_5$  and  $C_{10}H_{11}$ , disappears if we double these formulæ. The expressions  $C_4H_6$ ,  $C_8H_{10}$ ,  $C_{20}H_{22}$  correspond, like all the other hydrocarbons, to 4 volumes of vapour. In the absence of any decisive experiments upon the metamorphoses of the substances in question, it would be hazardous to adopt the latter formulæ in preference to those proposed by Drs. Kolbe and Frankland, unless some of the properties of these substances were found to countenance this change. Now I believe that the boiling-points of the compounds in question are certainly in favour of formulæ representing 4 volumes of vapour.

H. Kopp first pointed out the regular differences between the boiling-points of homologous liquids. As an average result from the observations made at the time when he wrote upon this subject, he has fixed upon the number 19 as the difference in the boiling temperatures of two analogous substances differing by  $C_2H_2$ . The numbers observed are often somewhat lower, but frequently also higher: benzol ( $C_{12}H_{16}$ ) boils at  $80^\circ$ , toluol ( $C_{14}H_{12}$ ) at  $108^\circ$ , the difference being  $28^\circ$ ; cumol ( $C_{18}H_{12}$ ) boils at  $148^\circ$ , cymol at  $175^\circ$ , difference  $27^\circ$ . I readily admit that our knowledge respecting boiling-points is still very deficient; yet the existence of a regularity like that observed by Kopp for a certain range of the thermometer cannot be denied. Now let us consider the boiling-points of the radicals hitherto observed. Methyl and ethyl, being gases at the ordinary temperature, may be left out of consideration. Valyl, obtained, in the electrolysis of valeric acid, boils at  $108^\circ$ ; amyl, as originally produced in the reaction of zinc upon iodide of amyl, and lately obtained by Messrs. Gosleth and Brazier in the electric decomposition of caproic acid, boils at  $155^\circ$ ; and, lastly, caproyl, if we may represent by this term a substance likewise produced by Messrs. Gosleth and Brazier in the analogous decomposition of cœnanthyllic acid, boils at  $202^\circ$ .

Name.	Formula.	Boiling-point.	Difference.
Valyl . . .	$C_8H_9$	$108^\circ$	47
Amyl . . .	$C_{10}H_{11}$	$155^\circ$	
Caproyl . . .	$C_{12}H_{13}$	$202^\circ$	47

\* Chem. Soc. Qu. J. III, 17.

The anomalous differences exhibited by the boiling-points in question, amounting actually in these instances for an elementary difference of  $C_2 H_2$  to nearly the double of the maximum ever observed, disappear at once if we adopt formulæ representing 4 volumes of vapour, as may be seen from the following conspectus, in which the boiling-points of the missing terms are assumed to be half way between those of their neighbours.

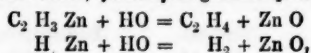
Name.	Formula.	Boiling-point.	Difference.
Valyl . . .	$C_{16} H_{18}$	108°	23
	$C_{18} H_{20}$	131·5°	
Amyl . . .	$C_{20} H_{22}$	155°	23
	$C_{22} H_{24}$	178·5°	
Caproyl . . .	$C_{24} H_{26}$	202°	23

The boiling-points are certainly in favour of the higher formulæ, so much indeed, that I believe, had these substances first been met with in coal-gas naphtha, or in the tarry liquids obtained in various processes of distillation, few chemists would have adopted other than 4-volume formulæ, unless they had been in the possession of additional information respecting their deportment. The formulæ representing 2 volumes of vapour derive, in fact, their chief support from the remarkable circumstances under which these substances originate. Hydriodic acid and zinc yield iodide of zinc and hydrogen; in the same manner, it would appear, the iodide of an alcohol-radical gives rise to the formation of iodide of zinc and the alcohol-radical.

There is decidedly a most striking parallelism; nevertheless there is a certain deficiency in the analogy, inasmuch as we do not by the action upon zinc of the hydrogen-acids obtain a compound of zinc and hydrogen corresponding to zinc-methyl.\*

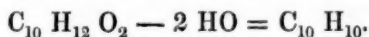
However, nobody will deny that the mode of formation of a compound must always be considered as a most important element in the construction of its formula, and in the case before us that mode of formation appears to be certainly in favour of the lower formulæ.

\* The existence of other metallic hydrides, as exemplified in the hydrogen-compounds of arsenic and antimony, induced me to study the action of *dry* hydrochloric acid upon zinc exposed in a combustion-tube to the *lowest* temperature at which the reaction took place; hydride of zinc, if it followed the deportment of zinc-methyl, would, when coming in contact with water, yield hydrogen and protoxide of zinc,



and might, in consequence of this decomposition, have escaped observation; however, the gas obtained in the above reaction, even when collected in perfectly dry vessels, was found to be free from zinc.

Nevertheless it would not be difficult to adduce many cases in which an entire reliance upon the mode of formation has led to the construction of formulæ which had subsequently to be rejected when other methods of investigation were applied to the same question. Shortly after the discovery of amyl-alcohol, M. Cahours\* examined the action of anhydrous phosphoric acid upon fusel-oil; he obtained a hydrocarbon boiling at  $160^{\circ}$ , which was immediately considered as the olefiant-gas term of the amyl-series,  $C_{10}H_{10}$ . Nothing appeared simpler than the formation of this body:



The density-determination, made by the same chemist, proved that the hydrocarbon in question was represented by 2 volumes of vapour; and M. Cahours characteristically remarked at that period, that the evident parallelism of the ethyl- and amyl-series was interrupted by the anomaly presented in the condensation of the elements in this hydrocarbon, olefiant gas, the corresponding term of the ethyl-series, being represented by 4 volumes. However, only a few years elapsed, when M. Balard, in studying this reaction on a larger scale, and using chloride of zinc as an agent of dehydration, discovered the actual olefiant-gas term  $C_{10}H_{10}$ , the true amylene boiling at  $39^{\circ}$ , and corresponding, like olefiant gas, to 4 volumes of vapour.

M. Balard showed that Cahours' hydrocarbon, which now assumed the name of paramylene, might be represented by



(corresponding to 4 vols. of vapour), a formula agreeing perfectly with its boiling-point. The same chemist found that in this reaction, in addition, even a third member of the same family, metamylenes,



is formed, the formula of which is likewise represented by 4 volumes of vapour.

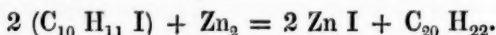
A series of perfectly analogous remarks applies to the hydrocarbons derived from acetone, by the elimination of water, under the influence of sulphuric acid. Mesityl is far from being represented by the formula which its discoverer assumed, who was guided by the supposed analogy of his product with olefiant gas. The boiling-point of the body being far too high for the assumed formula, the study of a series of its metamorphoses readily showed that its equivalent is actually treble that represented by the original formula. In the same manner, I might adduce the change which has been

\* Ann. Ch. Phys. [2] LXX, 81.

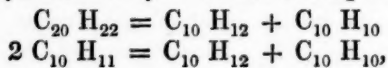
made in the formula of acetone itself,—the original expression of which was doubled, in consequence both of its deportment with reagents and its vapour-density.

It would not be difficult to quote a great number of cases exhibiting, in a similar manner, the tendency possessed by atoms of inferior order to be polymerized into molecules of a higher equivalent; and in no group of bodies, perhaps, does this inclination prevail to a greater extent, than among the alcohol-compounds.

Hence it would not appear a very unusual mode of decomposition, if we assume that, under the influence of zinc, 2 atoms of the hypothetical radical amyl unite to produce the hydrocarbon  $C_{20}H_{22}$ ,



This equation, in fact, would be satisfactory in every respect; it would be in accordance with the observed deportment of the body, with the usual mode of condensation of hydrocarbons, with the boiling-point,—and lastly, it would be even more in accordance with the formation of the secondary products of decomposition, namely, of amylene and hydride of amyl. Of the two equations,



the former is certainly better supported by analogy, although I do not lay much stress upon this point.

The admission of the doubled formulæ would, moreover, remove another difficulty, the discrepancy exhibited by the boiling-points of amylene, hydride of amyl, and amyl.

		Boiling-point.
Amylene	. . . $C_{10}H_{10}$	39°
Amyl	. . . $C_{10}H_{11}$	155°
Hydride of amyl	. . $C_{10}H_{12}$	30°

It appears strange, at the first glance, that the boiling-point of  $C_{10}H_{10}$ , should be raised more than 100° by the assimilation of 1 equivalent of hydrogen, whilst we usually find that the addition of hydrogen depresses the boiling-point; and again that in amyl the boiling-point should be depressed, even in a more striking manner, by its combining with the same amount of hydrogen. But I do not attach great importance to this point, inasmuch as the formulæ of these bodies, corresponding to different volumes, cannot well be compared with each other. Moreover, it is but right to state, that we are not very well acquainted with the influence of hydrogen on boiling-points; thus the boiling-point of bromine is considerably

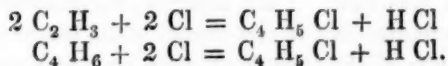
higher than that of hydrobromic acid, whilst on the other hand, hydrocyanic acid boils at a higher temperature than cyanogen itself.

The metamorphoses of the radicals, from which the most decisive evidence in favour of one or the other formula might be obtained, have as yet been studied but very imperfectly. The facts, however, with which we have hitherto become acquainted, are by no means in opposition to the higher formulæ.

Dr. Kolbe believes that the product obtained by distilling valyl with nitric acid, contains nitro-butyric acid; the liquid resulting from the action of nitric acid on amyl presents, according to Dr. Frankland, a powerful odour of valeric acid. These observations are perfectly in accordance with theory. The respective radicals pass over into the hydrated oxides of amyl and valyl, which, under the continued influence of the powerful oxidizing agents, yield their correlative acids.

Admitting that these acids are actually generated—which is still to be proved by more decisive experiments—I think that their formation is perfectly reconcileable with the doubled formulæ. We know that the action of nitric acid upon oleic acid gives rise to all the acids  $C_n H_n O_4$ , from capric downwards. We have no difficulty in converting the higher terms of this series into lower ones, *e.g.* pelargonic acid, into caprylic, cœnanthyllic, and even caproic acid. There is no reason why the carbohydrides  $C_{20} H_{22}$ , or  $C_{16} H_{18}$ , should not yield all the acids containing a smaller number of carbon-equivalents, and among these, valeric and butyric acids. Cymol and cumol are converted, under the influence of nitric acid, the former  $C_{20} H_{14}$  into toluyllic acid  $C_{16} H_8 O_4$ , the latter  $C_{18} H_{12}$  into benzoic acid  $C_{14} H_6 O_4$ .

The action of chlorine, which affords perhaps the simplest method of controlling formulæ, has been studied as yet only in one individual case. The results which Kolbe and Frankland obtained by acting with chlorine upon methyl derived from the decomposition of cyanide of ethyl with potassium, are highly remarkable. This gas yields under these circumstances, hydrochloric acid and a new chlorinated body represented by the formula  $C_4 H_5 Cl$ , which coincides with that of chloride of ethyl. The following equations represent the reaction according as we take either the formula  $C_2 H_3$ , or  $C_4 H_6$ .



The far greater simplicity of the second equation is evident: it has not escaped Mr. Frankland, who suggests that the methyl obtained

by the above process, is different from the true methyl, obtained by acting with zinc upon iodide of methyl or in the electrolysis of acetic acid, with which it would be only isomeric. An actual difference between the two substances is not yet proved by experiment.

As the question stands at present, two views have been enunciated respecting the bodies obtained by Drs. Kolbe and Frankland. The one view assumes the existence of two groups of bodies, one embracing the alcohol-radicals, and another containing the homologues of marsh gas, the former corresponding to 2, the latter to 4 volumes of vapour.

According to this view we have the following series :

Methyl	C <sub>2</sub> H <sub>3</sub>	Formene	C <sub>2</sub> H <sub>4</sub>
Ethyl	C <sub>4</sub> H <sub>5</sub>	Acetene	C <sub>4</sub> H <sub>6</sub>
Propyl*	C <sub>6</sub> H <sub>7</sub>		C <sub>6</sub> H <sub>8</sub>
Valyl (Butyl)	C <sub>8</sub> H <sub>9</sub>		C <sub>8</sub> H <sub>10</sub>
Amyl	C <sub>10</sub> H <sub>11</sub>	Caproene	C <sub>10</sub> H <sub>12</sub>
Caproyl	C <sub>12</sub> H <sub>13</sub>		C <sub>12</sub> H <sub>14</sub>

The other view considers all these substances as members of the same group as homologues of marsh gas (formene), and arrives at the following series :

Formene	C <sub>2</sub> H <sub>4</sub>	
Acetene	C <sub>4</sub> H <sub>6</sub>	Methyl?
	C <sub>6</sub> H <sub>8</sub>	
Valerene	C <sub>8</sub> H <sub>10</sub>	Ethyl?
Caproene	C <sub>10</sub> H <sub>12</sub>	Hydride of Amyl.
	C <sub>12</sub> H <sub>14</sub>	
	C <sub>14</sub> H <sub>16</sub>	
Pelargene	C <sub>16</sub> H <sub>18</sub>	Valyl?
	C <sub>18</sub> H <sub>20</sub>	
Caprene	C <sub>20</sub> H <sub>22</sub>	Amyl?
	C <sub>22</sub> H <sub>24</sub>	
Laurene	C <sub>24</sub> H <sub>26</sub>	Caproyl?

In the preceding pages, I have pointed out that the boiling-points of the radicals appear to me to speak for formulæ with 4 volumes of vapour; it now remains to be seen whether other experiments will come to the assistance of this view. I am, however, by no means prepared to say, whether, as represented in the second table, the so called radicals are actually bodies of the same properties as marsh gas; that they

\* This name might be given to the hydrocarbon obtained by Dr. Kolbe in the electrolysis of butyric acid; its examination is not yet completed.



are homologues of that body as is assumed in MM. Laurent and Gerhardt's interesting suggestion.

If we bear in mind the endless isomerisms prevailing in the department of organic chemistry, and especially among the hydrocarbons, witness the large family  $C_{20}H_{16}$ , we may perhaps assume that the so-called radicals, although presenting the same state of condensation, are only isomeric with the homologues of marsh gas, that they may exhibit an isomerism, similar to that of cumol and mesitolol. The latter view receives some support from the fact that methyl (acetene) when treated with chlorine, yields, not chloride of ethyl, but a compound isomeric with it, whereas if viewed as an homologue of marsh gas, it might be expected to give rise to the production of the former. This important experiment should be repeated.

If the preceding considerations lead us to adopt a view respecting the substances described under the names of methyl, ethyl, &c. which to a certain extent differs from that of their discoverers, if we cannot admit that the bodies in question actually represent the molecules which, as conceived by the electro-chemical theory, by the assimilation of 1 equivalent of chlorine, bromine, iodine, &c. give rise to the formation of the corresponding ethers, we are far from denying a most intimate relation of these compounds to the alcohols from which they are derived. This relation is sufficiently indicated by their mode of generation. These radicals it would appear, stand to the alcohols in a similar position as benzile and stilbene do to the benzoyl-group, or as the acetones stand to their mother-acids. All these substances are formed by the fusion of several organic molecules which split again under the influence of powerful agents, compounds of the original order being reproduced. The benzoyl-type when passing into benzile or stilbene, is polymerized into  $C_{23}H_{10}O_4$  and  $C_{28}H_{12}$ , which, under the influence of oxidizing agents, again return to the original series, oil of bitter almonds and benzoic acid being formed. Similarly, by converting acetic acid into acetone, we pass into a higher series, from which we step down again by acting with oxidizing agents upon the latter compound, which is reconverted into acetic acid. In an analogous manner, the so-called alcohol-radicals might give rise to the reproduction of the acids belonging to the original alcohols.

Should experiment, however, prove that the so-called alcohol-radicals are actually the homologues of marsh gas, as supposed by Messrs. Laurent and Gerhardt, these substances, although losing the prestige of radicals in the conception of the electro-chemical

theory, would certainly not present less interest. Chemists know the remarkable manner in which the researches of Dumas, Regnault, and Melsens, have linked the methyl-series to marsh gas, and the facility with which we pass from marsh gas over to chloride of methyl. We have a right to expect that the higher homologues of marsh gas will exhibit a similar deportment. If this be actually the case, the action of chlorine upon ethyl would place the whole series of the butylic alcohol at our disposal; in fact we should have discovered a general method of forming the homologues of common alcohol, and this series, presenting as yet so many gaps, would ere long be as complete as the parallel group of the fatty acids.

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May 6, 1850.

THE PRESIDENT in the Chair.

J. S. Brazier, Esq., W. F. Doyme, Esq., and Henry Deane, Esq., were elected Fellows of the Society.

The following presents were announced:

"Transactions of the Royal Scottish Society of Arts, Vol. III. Part IV :—" from the Society.

"The Pharmaceutical Journal, for April :—" from the Editor.

"Bauman's Medical Chemistry :—" from the Author.

"The Quarterly Journal of the Geological Society, for May, 1850 :—" from the Society.

A Paper, by Professor Wöhler, was read "On the Nitride of Boron." See p. 167.

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May 14, 1850.

ROBERT PORRETT, Esq., Treasurer, in the Chair.

The following presents were announced:

"An Account of certain Chemical and Microscopical Researches on the Blood, Excretions, and Breath in Cholera," by Thornton J. Herapath, Esq. : from the Author.

"The Collected Works of Sir Humphry Davy :—" from Dr. A. W. Williamson.

"The Pharmaceutical Journal, for May :—" from the Editor.

The following Papers were read :

XVII.—*On Chlorophosphuret of Nitrogen and its Products of Decomposition.**By J. H. GLADSTONE, PH. D.*

## PART. I.

A crystalline body containing phosphorus, nitrogen, and chlorine, was discovered by Wöhler and Liebig during their investigation of the compounds of nitrogen and phosphorus.\* It was slightly examined by its discoverers, and a partial analysis was made, from which was deduced the probable formula  $P_3 N_2 Cl_5$ . "Chlorphosphorstickstoff" was the name given to this substance, which has been translated by Kane:—"Chlorophosphuret of nitrogen." I am not aware that any chemist has since even prepared the body in question; but I have lately submitted it to a complete investigation, and shall now detail a portion of my results.

In the paper upon the compounds of phosphorus and nitrogen, which I had the honour to read before this Society last year,† chlorophosphuret of nitrogen was mentioned as invariably formed when pentachloride of phosphorus is saturated with ammoniacal gas. That its production does not depend upon any trace of moisture accompanying the ammonia, I established by passing the gas through tubes five feet in length, filled with sticks of potash, when exactly the same result was obtained. I found it also produced when pentachloride of phosphorus containing some terchloride was subjected to the action of ammoniacal gas; as also when the chloride was but imperfectly saturated with the gas. Thus it seems an invariable concomitant of the action of dry ammonia upon pentachloride of phosphorus. When the terchloride of phosphorus is saturated with ammoniacal gas, no trace of this substance is produced.

When thus prepared, it is mixed with a large amount of chloride of ammonium, and Gerhardt's "Chlorophosphamide." In order to separate it from these, the dry mass may be agitated with ether, which dissolves out the chlorophosphuret of nitrogen, leaving the other bodies. The ethereal solution will again yield crystals on evaporation; but as a secondary reaction is liable to take place between the ether and the chlorophosphuret, the following method of purification is to be preferred. The white mass resulting from the action of ammonia upon the pentachloride of phosphorus is placed in

\* Ann. Ch. Pharm. XI.

† Chem. Soc. Qu. J. II, 121.

a capacious retort, half filled with water, and the whole is brought into brisk ebullition; the chlorophosphuret of nitrogen melts, rises to the surface of the liquid, is volatilized along with the vapour of water, and condenses again in the neck in a state of purity.

As it requires a long time to saturate the pentachloride of phosphorus, and as the amount of the crystalline body produced is very small proportionally, this is a tedious process. Liebig found that the same could be effected by passing the vapour of pentachloride of phosphorus over chloride of ammonium, heated almost to the point of sublimation, in a glass tube three feet long, in a combustion furnace. Impure phosphuret of nitrogen is formed, torrents of hydrochloric acid are given off, and chlorophosphuret of nitrogen condenses in a receiver attached to the combustion tube. This is the process which I prefer; but I have found it expedient to modify it in some degree. One part of pentachloride of phosphorus is mixed with 2 parts of well dried chloride of ammonium, in a Florence flask, which may be half filled with the mixture. A series of two or more receivers is attached by means of tubes and perforated corks. The first receiver should be dry, and kept cool; the last should contain a considerable quantity of water. Heat is then applied to the flask, either by means of a large flame of a spirit lamp, or by glowing charcoal. The pentachloride of phosphorus gradually sublimes, combining with the chloride of ammonium, which becomes red at first, and is afterwards converted into a light brown substance, wholly free from soluble chloride, but retaining the original shape of the pieces. Chlorophosphuret of nitrogen sublimes. In the first receiver condenses a limpid liquid, with perhaps a small quantity of a white powder; whilst the hydrochloric acid gas is absorbed by the water in the last receiver, and a little chlorophosphuret is also deposited there. When no more pentachloride of phosphorus remains undecomposed, the flask may be suffered to cool, and the chlorophosphuret of nitrogen contained in it may be separated from the other matters by either of the processes above detailed.

The liquid condensed in the first receiver is colourless, and fumes in the air, emitting a pungent odour. When poured into water, it does not mix, but sinks to the bottom; after the lapse of a minute or two, violent chemical action ensues, the liquid disappears, chlorophosphuret of nitrogen remains in its place, and the water holds in solution hydrochloric and phosphoric acids. No permanently elastic gas insoluble in water is evolved during this reaction. If the liquid under consideration be heated, a large quantity of hydrochloric acid

is given off. A portion was taken and heated in a water-bath till the gas ceased to be evolved; the temperature was then raised, and at  $116^{\circ}\text{C}$ . ( $240.8^{\circ}\text{F}$ .) the liquid distilled over. When the thermometer began to rise rapidly, the distillation was stopped, and a liquid remained which deposited a quantity of crystalline chlorophosphuret of nitrogen on cooling. The distilled liquid was decomposed by water: only a minute trace of the crystalline body was left; and the hydrochloric and phosphoric acids were precipitated in the ordinary way.

1.2025	grms. of substance yielded
3.402	„ „ chloride of silver, and
0.870	„ „ phosphate of magnesia.

These numbers reckoned to 100 parts are:—

Phosphorus . . . . .	20.42
Chlorine . . . . .	69.80

evidently indicating oxychloride of phosphorus,  $\text{P Cl}_3 \text{O}_2$ , which requires:\*

Phosphorus . . . . .	32.0	20.71
Chlorine . . . . .	106.5	68.93
Oxygen . . . . .	16.0	10.36
	<hr/>	<hr/>
	155.5	100.00

The liquid in the first receiver then is merely oxychloride of phosphorus saturated with hydrochloric acid, and holding in solution a variable quantity of chlorophosphuret of nitrogen. The formation of the oxychloride must be regarded as accidental. It arises from the access of air to the pentachloride of phosphorus during its preparation; from the hygroscopic moisture, which it is difficult to remove completely from the chloride of ammonium employed; and, perhaps, also from the action of vapour of pentachloride of phosphorus upon the cork.

The amount of chlorophosphuret of nitrogen obtained by any of the processes just described, bears but a very small proportion to the pentachloride of phosphorus employed—not more, I believe, than about 6 per. cent. The quantity appears very uniform.

\* The slight excess of chlorine arises, in all probability, from a small amount of hydrochloric acid still retained by the liquid.

## PROPERTIES OF CHLOROPHOSPHURET OF NITROGEN.

Chlorophosphuret of nitrogen (at ordinary temperatures) is a solid crystalline body. It melts at about  $110^{\circ}$  C. ( $230^{\circ}$  F.) into a clear liquid, which enters into ebullition at about  $240^{\circ}$  ( $464^{\circ}$  F.) When immersed, however, in boiling water, it acquires a semi-fluid consistence; and I have observed, that when liquefied, and suffered to cool quietly, the temperature will sink below  $100^{\circ}$  C. without congelation taking place. Upon agitating it, when in this state, the whole becomes a mass of crystals, while the thermometer rises, from evolution of latent heat. The form of the crystals, as obtained by sublimation, is that of a rhomboid, of which the obtuse angle measures  $131^{\circ}$  or  $132^{\circ}$ , the acute  $48^{\circ}$  or  $49^{\circ}$ : the acute angle of this rhomboid, either at one or both ends, is often truncated, when of course the angle formed is about  $114^{\circ}$ : the hexagonal prism is also found. When crystallized from alcohol, or from a mixture of alcohol and ether, the same forms appear, the hexagonal prism being common. By crystallization from ether, I have obtained it in the form of beautifully defined hexagonal pyramids, the bases of which are in fact the truncated rhomboid before mentioned, the angles being  $132^{\circ}$  and  $114^{\circ}$ . These pyramids are found attached base to base.

The specific gravity of crystalline chlorophosphuret of nitrogen is somewhat greater than that of water, but that of the fused compound is less.

At ordinary temperatures, the substance under consideration slowly evaporates; but when heated, it diffuses a dense vapour, having a somewhat agreeable, but quite peculiar odour. The taste of its solution in alcohol is of a bitter character.

Chlorophosphuret of nitrogen is not soluble in water; indeed, as observed by Liebig, it shows great indisposition to be wetted by that liquid, behaving in this respect like a fatty body. It is dissolved by alcohol or chloroform, and to a large extent by ether; it is likewise very soluble in bisulphide of carbon, and in oil of turpentine, benzol, and other hydrocarbons. Its solubility in oxychloride of phosphorus has already been incidentally remarked.

A decomposition which its solutions in ether and alcohol spontaneously undergo, will be reserved for after consideration.

The original discoverers of this substance remarked that it is totally unaffected by aqueous solutions of either acids or alkalis, and that fusion with hydrate of potash does not decompose it. I find, however, that if chlorophosphuret of nitrogen be brought in contact



with such reagents through the medium of one of its solvents, it is by no means so stable. Thus, if it be treated with alcoholic solutions of potash, soda, or ammonia, decomposition ensues, and chloride, with other salts of the alkali remain. Even some metallic salts, when added to its solution in alcohol, will give rise to a double decomposition; thus, if nitrate of silver be added, an instantaneous formation of chloride of silver results.

The crystals under consideration may be sublimed without alteration in an atmosphere of hydrogen or hydrosulphuric acid gas. When heated with iodine, they are equally unaffected.

Powerful oxidizing agents attack chlorophosphuret of nitrogen, and give rise to the formation of phosphoric acid. Thus, when its vapour is passed over chromate of lead or metallic oxides—for instance, oxide of copper, at a red heat—it is decomposed, nitrous fumes being at the same time evolved. Nitric acid itself has no action upon the crystals, unless it be fuming, and at an elevated temperature: yet, if a solution in alcohol, or oil of turpentine, be employed, the substance is much more readily attacked by the acid in question.

Metals themselves, at a high temperature, exert a decomposing influence upon the vapour of chlorophosphuret of nitrogen, a fact observed by Wöhler and Liebig. Thus, if it be heated in a tube in contact with metallic silver, chloride of silver appears to be formed, together with some salt equally insoluble in nitric acid, and ammonia: a little white sublimate is also formed, which is soluble in water and contains chlorine. Again, if a bright piece of silver be immersed in an ethereal solution of chlorophosphuret of nitrogen in a closed vessel, it soon becomes coated with an incrustation of chloride of silver and the insoluble salt before-mentioned: after the lapse of some weeks, the decomposition will be complete, and the ethereal solution will have acquired an acid reaction. Similarly, if the substance in question be heated with potassium in an atmosphere of hydrogen gas, combination ensues, and chloride, together with some other salt of potassium, is formed. And again, if the crystals be dissolved in a pure hydrocarbon, and pieces of potassium be added and heat applied, combination takes place quietly.

#### COMPOSITION OF CHLOROPHOSPHURET OF NITROGEN.

From the decompositions above stated, it is evident that the crystalline body contains phosphorus, nitrogen, and chlorine. As

it is produced without the presence of air or moisture, and as the pentachloride of phosphorus, and the ammonia or chloride of ammonium, from which it is formed, are both free from oxygen, it is sufficiently evident that that element cannot enter into the composition of the crystals. In order to satisfy myself as to the presence or absence of hydrogen in this compound, I performed the following experiments. 1st. A weighed portion was burnt with chromate of lead, and the water was collected as in the ordinary process of organic analysis, metallic copper being placed in the anterior portion of the tube, and extraordinary precautions being taken that every material employed should be perfectly dry.—2nd. A long combustion-tube was filled with, in the first place, a weighed portion of the crystalline body, then several inches of copper turnings and reduced copper, afterwards some chromate of lead, separated from the former by a plug of asbestos, and then again copper-turnings. To the combustion-tube was attached a small tube containing sticks of caustic potash, and connected with it was one of Will's nitrogen apparatuses partially filled with dilute hydrochloric acid. Combustion was performed as usual. So small a trace of water or ammonia was obtained in either instance, as to preclude the belief that hydrogen forms a constituent of the crystalline body submitted to experiment.

The original investigators of this substance attempted an elementary analysis of it. The method adopted by them was that of decomposing the chlorophosphuret in a tube filled with metallic iron. The gas given off was collected and estimated as pure nitrogen; whilst the chloride of iron contained in the tube was washed out, and the chlorine precipitated as silver-salt. No attempt was made to estimate the phosphorus. The results were :

Nitrogen . . . .	11·2	10·1	97·2 per cent
Chlorine . . . .	58·3	”	”

From these numbers, Wöhler and Liebig deduced the formula  $P_3 N_2 Cl_5$ ; but, knowing that the estimations of nitrogen were fallacious, they put it forward with little confidence, thinking indeed that it might rather be  $P_2 N Cl_3$ .

I employed various methods of decomposition for the analysis of this substance, in order, if possible, to insure a correct result.

I. 0·5225 gram. of the crystalline body was dissolved in alcohol, and a solution of nitrate of silver was added. Chloride of silver continued to subside for a couple of days. At length, 1·246 gram. was obtained.

II. 0.457 grm. was decomposed by an alcoholic solution of ammonia. When evaporated to dryness, and redissolved in water, it yielded 1.0845 grm. of chloride of silver.

III. 0.1942 grm. was decomposed by an alcoholic solution of pure potash. This was evaporated to dryness, and heated to redness in a tube along with fresh potash. The ammonia evolved was collected in a hydrochloric acid apparatus, and yielded 0.327 grm. of platinum-salt. The fused mass, dissolved in dilute nitric acid, yielded 0.4647 grm. of chloride of silver, and 0.116 grm. of phosphoric acid, estimated by means of baryta.

IV. 0.2655 grm. was analysed in the same manner as the preceding, except that the fusion with potash was conducted in a short silver tube, inserted in an ordinary glass tube, to which the hydrochloric acid apparatus was attached. It yielded 0.390 grm. of platinum-salt, and 0.1552 grm. of phosphoric acid.

V. 0.4375 grm. was boiled with fuming nitric acid, in a vessel so contrived that the volatilized chlorophosphuret of nitrogen was returned again to the oxidizing liquid. The phosphoric acid, estimated by means of baryta-salt, was found to be 0.2615 grm.

VI. 0.2357 grm. was dissolved in alcohol and ether, and boiled with nitric acid in a vessel similar to that employed in the last experiment. Violent action of course ensued, and fresh alcohol and nitric acid were added, until it was believed that the oxidation of the chlorophosphuret was complete. The solution yielded 0.1595 grm. of phosphoric acid.

VII. 0.232 grm. was decomposed by passing it in vapour over red-hot oxide of copper. This method was found unsuitable for the determination of the chlorine, as a part of it enters into some insoluble compound, probably the dichloride. The mass remaining after the combustion was dissolved in hydrochloric acid; and the phosphoric acid was precipitated from a very ammoniacal solution as the ammonio-phosphate of magnesia. The portion undissolved by hydrochloric acid was then digested in strong nitric acid, and the phosphoric acid thus formed was precipitated as before. The second quantity of magnesia-salt being impure, was again fused with carbonate of potash, and the phosphoric acid reprecipitated. The whole amount of pyrophosphate of magnesia obtained was 0.2605 grm.

These results reckoned to 100 parts are:—

	I.	II.	III.	IV.	V.	VI.	VII.
Phosphorus	—	—	26.52	25.99	26.55	30.08	31.69
Nitrogen .	—	—	10.55	9.19	—	—	—
Chlorine .	58.83	58.53	59.02	—	—	—	—

This confirms the formula of the discoverers,  $P_3 N_2 Cl_5$ , which would require :—

Phosphorus	.	96.0	31.84
Nitrogen	.	28.0	9.29
Chlorine	.	177.5	58.87
		<hr/>	<hr/>
		301.5	100.00

The majority of my determinations of phosphorus, it will be seen, indicate an amount considerably below that required by theory; yet I think this presents no great obstacle. The compounds containing phosphorus and nitrogen, into which the chlorophosphuret of nitrogen is resolved, are themselves very difficult of decomposition, some unrecorded experiments, conducted by other methods, yielded estimations of phosphorus which were much smaller and unquestionably incorrect. From the amount of nitrogen and chlorine obtained, it is manifest that, if the crystals contain no other element than phosphorus beside these, such an amount as 26 or 27 per cent requires the addition of 4 or 5 to complete the 100 parts, (*vide* Experiment III, in which the sum of the three numbers is only 96.09). The 7th experiment does give a result coincident with theory; yet, unfortunately, from the difficulties attending it, I cannot lay much stress upon this determination. The method adopted in the 6th experiment is, I conceive, worthy of the greatest reliance, and that yields 30.08 per cent of phosphorus. Besides which, an indirect method of analysis, which will be detailed towards the close of this paper, afforded a determination of the amount of phosphorus equal to that required by the formula  $P_3 N_2 Cl_5$ .

#### AZOPHOSPHORIC ACID.

*Iron-salt.*—It has already been remarked that if chlorosulphuret of nitrogen be dissolved in alcohol, and potash or ammonia be added, decomposition instantly ensues. Now if this solution be evaporated to dryness, redissolved in water, and rendered perfectly neutral, it gives no precipitate on the addition of most metallic salts, thus proving that it contains no phosphoric acid. If however the neutral solution, or the solution rendered strongly acid, be boiled with a salt of sesquioxide of iron, a white flocculent precipitate speedily forms. It has the appearance of the ordinary phosphate of the sesquioxide of iron, but it is at once distinguished from that salt, by the two remarkable properties of being insoluble in dilute acids, but completely soluble in ammonia. When treated with a solution of

potash, this salt is immediately decomposed; sesquioxide of iron remains; and in solution is a potash-salt of the new acid, from which the iron-salt may again be formed by neutralization with acid, and the addition of any solution of that metal. Alkaline carbonates decompose it upon the application of heat. If it be fused with potash, ammonia is evolved; and the fused mass redissolved in acid and treated with ammonia, gives ordinary phosphate of iron. Strong sulphuric acid dissolves it, and decomposes it when warmed.

The action of heat upon this salt is remarkable. When dried at ordinary temperatures, or at  $100^{\circ}\text{C}$ ., it has a white or rather a light buff colour; but when heated to about  $330^{\circ}\text{C}$ . ( $572^{\circ}\text{F}$ .) it suddenly gives off vapour of water and ammoniacal gas, assuming a dark brown colour, while a small quantity of a white crystalline body also sublimes. This sublimate is soluble in water; when it is treated with a solution of nitrate of silver, a white precipitate is produced, which changes immediately to a clear orange-red; and shortly afterwards there is formed a quantity of black substance insoluble in ammonia, apparently reduced silver. The iron-salt gives off water preparatory to decomposition, even when previously dried at  $220^{\circ}\text{C}$ . ( $428^{\circ}\text{F}$ .)

Although this salt does not present itself in crystals, the fact of its being formed in decidedly acid solutions is a tolerable guarantee of its purity. I have prepared it at as low a temperature as  $46^{\circ}\text{C}$ . ( $114.8^{\circ}\text{F}$ .), but a higher degree of heat is desirable, so as to ensure a complete transformation. Analyses were effected by the following methods.

I. 0.2735 grm. of salt dried at  $100^{\circ}\text{C}$ ., was fused with pure hydrate of potash in the short silver tube mentioned above, inserted within a glass tube. The evolved gas was collected in Will's hydrochloric acid apparatus, and yielded 0.248 grm. of ammonio-chloride of platinum. The fused mass was then dissolved in water, filtered, and the phosphoric acid in the solution was precipitated as magnesia-salt. The undissolved oxide was fused with a mixture of the carbonates of potash and soda, to separate any phosphoric acid which might still be combined with it, following the directions given by Rose in his paper on the estimation of phosphoric acid, in *Pogg. Ann.* Part II. for last year. The amount of sesquioxide of iron obtained was 0.0943 grm. The additional pyrophosphate of magnesia obtained was 0.005 grm., to be added to the previous amount 0.2373 grm.

II. 0.215 grm. of salt dried at  $70^{\circ}\text{C}$ . ( $158^{\circ}\text{F}$ .) weighed only 0.205 grm. when dried at  $120^{\circ}\text{C}$ . ( $248^{\circ}\text{F}$ .). This was decomposed, *per se*, by heat in a glass tube, to which was attached a tube containing sticks of caustic potash. The loss of weight during the process

of heating was 0.0405 grm.; the amount of water collected was 0.0145 grm. The mass remaining in the tube was fused with caustic potash; and the ammonia evolved, collected in a hydrochloric acid apparatus, yielded 0.0215 grm. of platinum-salt. As the substance had been fused with potash in a glass tube, it was very probable that some other oxides beside sesquioxide of iron existed in the alkaline mass: for this reason, the method suggested by Rose for the separation of mixed oxides from phosphoric acid, by means of nitric acid and mercury, was adopted. The amount of sesquioxide of iron was found to be 0.0695 grm.; that of pyrophosphate of magnesia obtained was 0.179 grm.

III. A portion of iron-salt, which had been allowed to remain seven days *in vacuo* over sulphuric acid, weighed 0.254 grm.; when dried at between 120° and 130° C. (248°—266° F.) it parted with moisture, and weighed only 0.2422 grm. The salt heated as in the preceding experiment lost 0.0475 grm. The amount of water collected in the tube filled with sticks of potash was 0.029 grm.; the ammoniacal gas given off, and collected in a hydrochloric acid apparatus annexed to the tube for absorbing the moisture, yielded 0.110 grm. of platinum-salt. The remaining mass was fused in the silver tube, and evolved gas, which afforded 0.022 grm. of pure chloride of ammonium. The amount of sesquioxide of iron in the alkaline mass was 0.0835 grm.

IV. 0.2112 grm. of iron-salt dried at a temperature of 160° C. (320° F.), heated as in preceding experiments, showed a loss of 0.0393 grm. The amount of water collected was 0.025 grm.; that of platinum-salt was 0.0755 grm. The salt was fused with potash as before, but the amount of ammonia evolved was not correctly ascertained. The resulting mass was dissolved in acid; and, since I had learnt by experience that the entire amount of phosphoric acid produced by the decomposition of such substances as these phosphorus compounds, is seldom if ever precipitated by magnesia-salt, the separation of the sesquioxide of iron from the phosphoric acid was effected as in the preceding cases, but the acid itself was estimated by means of baryta. The amount of sesquioxide of iron was 0.071 grm.; that of phosphoric acid 0.133 grm.

It will be evident from consideration of Experiments III. and IV., that some other gas besides ammonia and vapour of water is evolved when this iron-salt is heated. Thus:

	Water.	Ammonia.	Actual loss.
Exp. III.	0.029 + 0.0084 = 0.0374 not 0.0475		
Exp. IV.	0.025 + 0.0057 = 0.0307 „ 0.0393		



If we suppose that the ammonia did not exist as such in the iron-salt, which is of itself improbable, but that it was formed under the influence of heat by the combination of nitrogen with hydrogen, which was itself obtained from the decomposition of a portion of the water; and that the oxygen thus set free was evolved along with the other gases, we have a theoretical loss coinciding very nearly with that actually found.

	Water.	Nitrogen.	Decomposed water.	Theoretical loss.	Actual loss.
Exp. III.	0.029	+ 0.0069	+ 0.0015 × 9	= 0.0494	0.0475
Exp. IV.	0.025	+ 0.0047	+ 0.0010 × 9	= 0.0387	0.0393

If we calculate the ammonia evolved in the second experiment on the same principles as this, we have, assuming  $x$  as the amount of hydrogen in the water that was decomposed,

$$0.0145 + \frac{14x}{3} + 9x = 0.0405,$$

from which it appears that the quantity of hydrogen combined to form ammonia was 0.0019 grm.; and the nitrogen with which it united itself must have been 0.009 grms.

The percentage amount of the elements, reckoned from the numbers obtained in the four experiments recorded above, is subjoined. The weight of iron-salt, as dried at a temperature not lower than 100° C., is assumed as the basis of the calculation; and I have also added, in brackets, the amount of hydrogen and nitrogen, in the second experiment, as estimated, on theoretical grounds, from the loss.

	I.	II.	III.	IV.
Sesquioxide of iron	34.48	33.90	34.47	33.62
Phosphorus . .	25.05	25.07	—	27.93
Nitrogen . . .	5.67	[5.07]	5.24	—
Hydrogen . . .	—	[1.70]	1.94	1.81

These numbers accord sufficiently with those deduced from the formula  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{NO}_5 \cdot 4 \text{HO}$ .

Sesquioxide of iron . . . .	80	34.19
Phosphorus . . . . .	64	27.35
Nitrogen . . . . .	14	5.98
Hydrogen . . . . .	4	1.71
Oxygen . . . . .	72	30.77
	<hr/>	<hr/>
	234	100.00

If we assume, as the basis of our calculation, the weight of iron-salt as dried at  $70^{\circ}\text{C}$ ., or at ordinary temperatures *in vacuo*, and add the amount of water driven off at a higher degree of heat, we have, for the second and third experiments :

	I.	II.
Sesquioxide of iron . . .	32.33	32.87
Phosphorus . . . . .	23.92	—
Nitrogen . . . . .	[4.83]	5.00
Hydrogen . . . . .	[2.13]	2.36

corresponding with the numbers deduced from the formula  
 $\text{Fe}_2\text{O}_3. \text{P}_2\text{N O}_5. 5 \text{HO} :$

Sesquioxide of iron . . . .	80	32.92
Phosphorus . . . . .	64	26.34
Nitrogen . . . . .	14	5.76
Hydrogen . . . . .	5	2.06
Oxygen . . . . .	80	32.92
	<hr/>	<hr/>
	243	100.00

In what light these 5 atoms of water are to be viewed, I know not. I have in vain sought the aid of powerful microscopes for any crystalline appearance in the precipitate. It seems also that one of the atoms must be regarded in a different manner from the four others, since it is driven off at the boiling-point of water, while the rest remain.

#### COMPOUND OF THE IRON-SALT WITH AMMONIA.

It has already been stated that the iron-salt is entirely soluble in ammonia. It gives a red solution, from which the iron-salt may be again precipitated by the addition of an acid. An attempt was made to obtain this compound salt in the dry state. An ammoniacal solution was carefully evaporated in a water-bath: it came out as a dark red mass, very soluble in water, but manifesting no disposition to crystallize. After being perfectly dried, it was treated with water, when it separated into two portions; the one soluble, containing ammonia, and giving a characteristic precipitate when treated with acid; the other like micaceous plates of the colour of red prussiate of potash, which appeared to be mainly sesquioxide of iron.

Similar salts of other oxides may be produced from the chlorophosphuret of nitrogen in the same manner as the iron-salt just described; but that is the only one, as far as I have observed, which will preci-

pitate from very acid solutions. Hence it is the salt upon the purity of which the greatest reliance can be placed, and I accordingly chose it for the most particular examination.

*Alumina-salt.*—This is prepared when a solution of alum is added to an aqueous solution of chlorophosphuret of nitrogen decomposed by ammonia and alcohol, which should be slightly acid to test-paper. No precipitate falls in the cold, but upon boiling the mixture, a white flocculent precipitate is formed. This is an alumina-salt similar to the iron-salt already investigated: when dry it is pulverulent: upon being heated in a test tube it becomes black, then again white, giving off ammonia, water, and a small quantity of the white sublimate mentioned as being also formed during the destruction of the iron-salt.

*Copper-salt.*—When sulphate of copper is added to the same slightly acid solution of chlorophosphuret of nitrogen, and the mixture boiled, a pale blue flocculent copper-salt precipitates. When heated, *per se*, this salt fuses, swells up, becomes black, and afterwards lighter in colour, and evolves ammonia, vapour of water, and the same white sublimate. It is wholly decomposed by a cold solution of potash.

An analysis was made. 0.2923 grm. of copper-salt dried at  $100^{\circ}\text{C}$ . was heated in the same manner as the iron-salt. The loss in weight was 0.0468 grm.; the amount of water collected was 0.030 grm.; that of platinum-salt obtained was 0.0172 grm. The remaining mass was then fused with potash. The amount of pure chloride of ammonium obtained from the evolved gas was 0.011 grm. The oxide of copper was separated from the phosphoric acid by fusion with alkaline carbonates, with the precautions recommended by Rose in the memoir already more than once referred to. It weighed 0.124 grm.

These numbers reckoned to 100 parts accord sufficiently with the formula,  $3\text{CuO} \cdot \text{P}_2\text{NO}_5 \cdot 5\text{HO}$ .

	Calculated.		Found.
Oxide of copper . . . .	119	42.20	42.42
Phosphorus . . . .	64	22.70	—
Nitrogen . . . .	14	4.96	4.72
Hydrogen . . . .	5	1.77	1.94
Oxygen . . . .	80	28.37	—
	<hr/>		
	282	100.00	

From the amount of water and ammonia evolved during the heating of this copper-salt, compared with the actual loss of weight, it

would appear that, unlike the iron-salt, a portion of the oxygen set free by the decomposition of water, was not given off along with the other gases.

Water.	Nitrogen.	Decomposed water.	Theoretical loss.	Actual loss.
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$0.030 + 0.0108 + 0.0024 \times 9 = 0.0624$  instead of  $0.0468$

Since the heated mass, after becoming black, became again white, it seems probable that the phosphuret of the metal, or some such compound—to which, without doubt, the black colour in these decompositions is owing—was oxidized by the free oxygen; and this will account for the decrease of weight being less than that expected.

*Silver-salt.*—If to a neutral solution in water of the salts obtained by the decomposition of chlorophosphuret of nitrogen by means of alcohol and ammonia, excess of nitrate of silver be added, a dense precipitate falls, consisting principally of chloride of silver. If this be shaken, and removed by filtration, and the solution be boiled, a bulky white precipitate forms. This salt, when collected and dried, has the appearance of a granular grey powder, little affected by light. When heated *per se*, it fuses, swells up greatly, and evolves the usual gases, becoming at the same time black, which is afterwards exchanged for a greenish colour.

A quantity was prepared for analysis by a different process. Some of the iron-salt was decomposed by a solution of potash in the cold; the resulting solution was neutralized by nitric acid, and nitrate of silver was added. The salt thus obtained was analysed in a similar manner to the preceding. It was dried at  $160^{\circ}$  C. ( $328^{\circ}$  F.), but it appeared to lose nothing between  $80^{\circ}$  C. ( $176^{\circ}$  F.) and that point, when it began to soften.

I.  $0.1385$  gm., heated *per se*, showed a loss in weight of  $0.005$  gm. The amount of water collected was  $0.0018$  gm.; that of platinum-salt obtained was  $0.0225$  gm. After fusion with potash, the amount of platinum-salt obtained was  $0.025$  gm. The alkaline mass dissolved in dilute nitric acid, and treated with hydrochloric acid, gave  $0.1075$  gm. of chloride of silver; and the phosphoric acid estimated by means of baryta-salt, was  $0.0429$  gm.

II.  $0.394$  gm. of a separate preparation, decomposed by dilute hydrochloric acid, yielded  $0.333$  gm. of chloride of silver.

These numbers reckoned to 100 parts yield:

	I.	II.
Oxide of silver . . .	67.15	68.39
Phosphorus . . .	13.79	—
Nitrogen . . .	2.17	—
Hydrogen . . .	0.36	—

From the amount of base, it would appear that the silver-salt is strictly analogous in composition to the copper-salt just described; and yet the amount of hydrogen obtained would rather indicate 2 atoms of water than 5. It must however be borne in mind, when estimating the value of these analytical results, that the varying quantity of white sublimate may always introduce an error, more or less great, in the determination of hydrogen.

Calculation from the formula  $3 \text{AgO} \cdot \text{P}_2 \text{NO}_5 \cdot 5 \text{HO}$  :

Oxide of silver . . .	348.9	68.16
Phosphorus . . .	64	12.50
Nitrogen . . .	14	2.73
Hydrogen . . .	5	0.98
Oxygen . . .	80	15.63
	<hr/>	<hr/>
	511.9	100.00

The comparison between the actual loss of weight in the first experiment, and that calculated from the amount of water and ammonia found, reckoning the whole oxygen to be evolved, is as follows :—

Water.	Nitrogen.	Decomposed water.	Theoretical loss.	Actual loss.
$0.0018 + 0.0014 + 0.0003 \times 9 = 0.0059$				0.005

**Lead-salt.**—The lead-salt may be prepared by similar methods. It is white and granular, when dry. If decomposed by heat, it decomposes itself in the same manner as the salts previously described. It is decomposed, not dissolved, by ammonia.

**Mercury-salt.**—Flocculent mercurial salts may be prepared from the potash-salt by double decomposition with either the subnitrate or protonitrate of mercury. That containing the suboxide is white, with a slight tinge of yellow. When heated *per se*, after being dried *in vacuo* it becomes black, water and ammonia and the white sublimate are given off; the mass fuses, and swells greatly, and metallic mercury eventually sublimes.

**Baryta-salt.**—This salt cannot be obtained in the pure state, by adding a solution of a baryta-salt to a neutral or slightly acid solution of decomposed chlorophosphuret of nitrogen. It may, however, be easily prepared, when the iron-salt is decomposed by a cold solution of potash, the resulting liquid neutralized by acid, and nitrate of baryta or chloride of barium added. The salt thus obtained is white and flocculent: when dried and heated *per se*, it gives off the same bodies as all the other salts of this acid which I have examined, becoming in the meantime of a dark brown colour.

The analysis was effected in the usual way.

I. 0.2195 grm. of baryta-salt, precipitated from a slightly acid solution, and dried at  $150^{\circ}$  C. ( $302^{\circ}$  F.), showed a loss of weight upon heating, of 0.0135 grm. The water collected was 0.0045 grm.; the platinum-salt obtained 0.069 grm. After fusion with potash, the platinum-salt obtained was 0.020 grm. The sulphate of baryta precipitated was 0.224 grm., and the pyrophosphate of magnesia produced was 0.137 grm.

II. 0.1487 grm. of baryta-salt, precipitated from a solution rendered slightly ammoniacal, and dried at  $150^{\circ}$  C., showed a loss of weight upon heating, of 0.0092 grm. The water collected was 0.005 grm.; the platinum-salt obtained 0.029 grm. After fusion with potash, the platinum-salt obtained was 0.033 grm. The sulphate of baryta precipitated was 0.1415 grm., and the pyrophosphate of magnesia produced was 0.0815 grm.

These numbers reckoned to 100 parts, accord best with the percentage deduced from the formula  $3 \text{ BaO} \cdot \text{P}_2 \text{ NO}_5 \cdot 2 \text{ HO}$ .

Calculated.		Found.	
		I.	II.
Baryta . . .	230 62.84	66.92	62.45
Phosphorus . .	64 17.49	17.63	15.47
Nitrogen . . .	14 3.82	2.55	2.62
Hydrogen . . .	2 0.55	0.64	0.63
Oxygen . . .	56 15.30	—	—
	<hr/> 366 100.00		

The salt analysed in the first experiment appears to have been impure.

The actual loss of weight upon heating the salt in each of these experiments, is a little less than that calculated from the amount of water and ammonia collected, supposing the whole of the oxygen set free to be given off as such. This must be ascribed to the same reason as in the case of the copper-salt.

Water.	Nitrogen.	Decomposed water.	Theoretical loss.	Actual loss.
0.0045 + 0.0043 + 0.0009		$\times 9 =$	0.0169	instead of 0.0135
0.0040 + 0.0018 + 0.00089		$\times 9 =$	0.0103	„ „ 0.0092

In glancing over these analyses, it will be remarked that the amount of nitrogen obtained, is in every instance below that required by theory, and in some cases the deficiency is very considerable. I believe this is solely due to the nitrogen not being entirely converted



into ammonia during the fusion with potash, and to the difficulty of collecting the whole quantity of gas then evolved. This opinion is supported by the fact, that, in the copper-salt, where the large amount of water permitted the nitrogen to be mostly given off as ammonia, when the salt was heated *per se*, the amount of nitrogen found very nearly equals that calculated from the formula; while in the baryta-salt, where the very small amount of water precluded much of the nitrogen being thus given off, the deficiency was far more considerable.

I have also prepared, by similar methods, compounds of this acid with the oxides of chromium, manganese, nickel, cobalt, zinc, cadmium, and tin, besides strontia, lime, and magnesia. All these present themselves as flocculent precipitates; and all are of a white colour, except the cobalt-salt, which is pink. No precipitate is obtained upon mixing a solution of the potash-salt with either a solution of bitartrate of antimony and potash, or a solution of terchloride of gold. If the iron-salt be decomposed by soda, and the alkaline salt thus obtained be rendered slightly acid, and a solution of bichloride of platinum be added, no precipitate results. I obtained, however, a compound containing this metal, when a mixture of the bichloride and potash-salt was evaporated to dryness. It was of a brown colour, insoluble in water, and soluble with difficulty in hydrochloric acid: when heated in a tube it assumed a swimming appearance, from the escape of gas; water was given off, together with a little white sublimate, and—not ammonia—but hydrochloric acid in considerable quantity. The substance in the tube became quite black, and afterwards brown, like spongy platinum. It is possible that this compound may contain potash.

*Potash-salt.*—The compounds of this acid with the alkalis, being soluble in water, cannot of course be obtained in a fit state for analysis in the same manner as the metallic salts. In order to obtain a pure potash-salt, some of the iron-compound was decomposed, by means of a quantity of the purest potash, not equivalent to the whole of the iron. The solution was neutral to test-paper, whilst a portion of the white salt unconverted into the red oxide of iron was a further guarantee that the whole of the caustic alkali had entered into a new compound. The filtered solution was evaporated *in vacuo* over sulphuric acid. It was hoped that a crystalline salt would thus be obtained, but it dried to a greenish gum-like mass, deliquescent in moist air, but insoluble in alcohol. It was analysed by the addition

of bichloride of platinum and free hydrochloric acid; but owing to the formation of the peculiar platinum-salt noticed above, it is doubtful whether the whole of the alkali was converted into the double chloride of platinum and potassium. Yet from 0.1243 grm. of the salt dried *in vacuo* there was obtained 0.272 grm. of double chloride, which is equivalent to

Potash—42.35 per cent.

Now the composition,  $3 \text{ KO} \cdot \text{P}_2 \text{NO}_5 \cdot 5 \text{ HO}$  would require

Potash—46.49 per cent,

a quantity not much larger.

*Ammonia-salt.*—When the lead-salt is decomposed by dilute ammonia, and the solution thus obtained is evaporated *in vacuo* over sulphuric acid, the ammonia-salt presents itself as a viscid mass, without showing the slightest tendency to crystallize. It is very soluble, both in water and in alcohol.

*Free acid.*—My first attempts to obtain this acid in the free state, were made by decomposing the copper-salt diffused through water, by means of a stream of hydrosulphuric acid; but a breaking-up of the liberated acid into simpler forms seemed always to ensue, at least after the lapse of a short time, it was resolved, under the influence of water, into compounds of ammonia with phosphoric or phosphorous acid. But on treating the silver-salt with dilute hydrochloric acid, a solution was obtained, from which the characteristic iron-salt could be readily produced. This was evaporated down, at first by heat, afterwards under the air-pump. Some crystals appeared, which however swelled and broke up, before the mass became perfectly dry. A semi-solid non-crystalline substance remained, which proved to be the acid in question. The acid thus obtained is deliquescent in moist air, readily soluble in water or alcohol, and slightly so in ether: its solution reddens blue litmus-paper, and has an agreeable acid flavour. It may be subjected to a high degree of heat without alteration; but, if heated on platinum-foil in the flame of a spirit-lamp, it fuses, blackens, and eventually rises in vapour. The salts already described may be prepared from it: thus, if it be treated with ammonia in excess, and a minute quantity of a solution of sulphate of sesquioxide of iron be added, not the slightest trace of sesquioxide appears, but the liquid assumes a clear red colour. This I esteem the most characteristic single test of the acid in question.

It appears, then, that we have here a peculiar acid resembling phos-

phoric acid, both in its terbasic character, and in the general physical and chemical character of its salts, but differing from phosphoric acid in constitution, since it contains one atom of phosphorus and one atom of nitrogen in addition to  $\text{PO}_5$ . Without reference to any particular theory, I shall simply denominate it *Azophosphoric acid*. A list of the salts analysed is annexed in the subjoined table for the purpose of comparison.

Salt.	Dried at	Composition.
Azophosphate of iron . .	below $100^{\circ}$ C.	$\text{Fe}_2 \text{O}_3 \cdot \text{P}_2 \text{NO}_5 \cdot 5 \text{HO}$
"    "    "    "	$100^{\circ}$ – $160^{\circ}$ C.	$\text{Fe}_2 \text{O}_3 \cdot \text{P}_2 \text{NO}_5 \cdot 4 \text{HO}$
"    of copper . .	$100^{\circ}$ C.	$3 \text{CuO} \cdot \text{P}_2 \text{NO}_5 \cdot 5 \text{HO}$
"    of silver . .	$100^{\circ}$ – $160^{\circ}$ C.	$3 \text{AgO} \cdot \text{P}_2 \text{NO}_5 \cdot 5 \text{HO}$
"    of baryta . .	$150^{\circ}$ C.	$3 \text{BaO} \cdot \text{P}_2 \text{NO}_5 \cdot 2 \text{HO}$
"    of potash .	Ord.tem. <i>invac.</i>	$3 \text{KO} \cdot \text{P}_2 \text{NO}_5 \cdot 5 \text{HO}?$

It occurred to me that the readiness with which the azophosphate of iron is produced from the chlorophosphuret of nitrogen, might be taken advantage of in the analysis of that substance, particularly in reference to the amount of phosphorus. A weighed portion of the crystals was therefore dissolved in alcohol, decomposed by ammonia, evaporated to dryness, and the resulting mass re-dissolved in water. An acid solution of sulphate of sesquioxide of iron was then added, and boiling was continued for an hour. The salt thus precipitated was collected on a weighed filter, and dried at  $100^{\circ}$  C. The filtered solution was evaporated to dryness, treated with a little hydrate of potash, re-dissolved in acid, and precipitated by ammonia. The mixture of phosphate and oxide of iron thus obtained was analysed by fusion.

0.2803 gram. of chlorophosphuret of nitrogen yielded :

0.180   "   "   azophosphate of iron, and

0.1435   "   "   pyrophosphate of magnesia.

Assuming that phosphorus constitutes 27.35 per cent. of azophosphate of iron, these results indicate

Phosphorus—32.00 per cent,

an estimation equalling, or rather just exceeding that required by the formula  $\text{P}_3 \text{N}_2 \text{Cl}_5$ : viz.,

Phosphorus—31.84 per cent.

In the present paper I have confined myself to a mere description and analysis of this crystalline body, the so-called "Chlorophos-

phuret of Nitrogen,"  $P_3 N_2 Cl_5$ ; and of a peculiar acid, with its salts, "Azophosphoric Acid,"  $P_2 NO_5$ . Upon the manner of formation of the first compound, and upon the reactions, by which the second is derived from it, I hope to enter at some future opportunity, when I anticipate laying before the Society some further products of the decomposition of chlorophosphuret of nitrogen, and among them some which will probably facilitate our understanding of the rational composition of the bodies here described.

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XVIII.—*On the Action of Chloride of Cyanogen upon Toluidine.*

By W. WILSON,

The perfect homology existing between toluidine and aniline left but little doubt respecting the deportment which the former alkaloid would exhibit, when exposed to the influence of chloride of cyanogen; still the discrepancies which we frequently observe between the various members of one series, especially if we rise on the scale of compounds, made it desirable to establish the behaviour of toluidine by experiment.

PREPARATION OF TOLUIDINE.

The preparation of toluidine is a process of considerable difficulty, inasmuch as the collateral hydrocarbon can be obtained only in comparatively small quantities. The formation of toluol has hitherto been observed in different processes, namely: in the distillation of tolu-balsam by Deville, its discoverer; in the distillation of dragon's blood (dracyl), by Boudault and Glenard; in the decomposition of toluyllic acid by Noad; and lastly it has been met with among the hydrocarbons of coal-tar naphtha by Mansfield.

I have tried all these methods in order to procure toluol in larger quantities, and I find that the source last-mentioned is that which yields this compound most easily and in greatest quantity;—only comparatively minute quantities being obtained by the other processes.

The best plan is to select the fraction distilling between  $100^{\circ}$  and  $120^{\circ}$  C., and to treat this portion with half its bulk of concentrated sulphuric acid. I am not prepared to say what substances are removed by this process; the fact is, however, that a constant boiling-point is more easily reached with, than without, the use of

sulphuric acid. In all cases, a series of tedious distillations is required, in order to accomplish this object. The boiling-point of toluol was found to be  $110^{\circ}$  C.

The conversion of toluol into nitro-toluol succeeds without difficulty in the usual manner. Nitro-toluol was found to boil between  $220^{\circ}$  and  $225^{\circ}$ , without decomposition.

Those chemists who have used Zinins' process for the amidation of nitro-compounds, are aware how difficult it is to effect the complete conversion of these substances when treated with sulphide of ammonium, especially if there is but 1 equivalent of hyponitric acid present. I have used in my experiments a solution of hydrosulphate of sulphide of potassium with which the nitro-toluol was repeatedly distilled. The advantages which the potassium-compound presents are very remarkable, not half the time being required as with sulphide of ammonium; moreover, the base, once formed, has no longer to be separated from the ammonia which, in the latter case, distils over with it.

The toluidine obtained in this manner, after having been several times crystallized, in the form of oxalate, and lastly, distilled with caustic lime, presents all the properties which its discoverers assigned to it.

#### PREPARATION AND ANALYSIS OF METOLUIDINE.

In subjecting toluidine to the action of chloride of cyanogen. I adopted, in the first place, the same arrangement that Dr. Hofmann had used in preparing melaniline, namely, a series of tubes, filled with the *dry* alkaloid, through which the chloride of cyanogen was drawn by means of an aspirator. I soon found, however, that the deportment of toluidine is by no means so simple as that of aniline under similar circumstances. The alkaloid being solid at ordinary temperatures, it was necessary to support the action from the very commencement by the application of heat, under the influence of which, unless it be very carefully applied, the newly formed hydrochlorate appears to undergo some farther metamorphoses. On this account I found it more convenient to introduce toluidine into a slightly bent tube, to diffuse it by a gentle heat into a thin layer over the sides, and then to expose this increased surface to the action of the gas. In this manner the heat evolved during the reaction was sufficient to keep the substance in a state of fusion. As soon as the action had ceased, the resinous mass, consisting almost entirely of hydrochlorate of the new base, was dissolved in water to which a small quantity

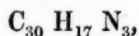
of hydrochloric acid had been added. On mixing the filtered solution with potassa, a white precipitate took place which was boiled for some time with the potassa, in order to distil off with the aqueous vapours small quantities of toluidine which might have escaped the action. The residue was thrown upon a filter, separated by washing, from the chloride of potassium, and recrystallized from alcohol.

From this solution, the new base, which I propose to call *Metoluidine*, a name corresponding to melaniline, is deposited in small crystalline plates. It crystallizes better from a mixture of alcohol and water, but by no means with the same facility as melaniline; this substance is but slightly soluble in water, but somewhat more so at the boiling-temperature.

I have established the composition of metoluidine by analyses of the base itself, and by that of the platinum-salt :

0.2201 grm. of base gave  
0.6048 „ of carbon, and  
0.1454 „ of water.

These numbers, together with those obtained with the platinum-salt, lead to the formula



which requires the following values :

	Theory.		Experiment.
30 equivs. of Carbon . . .	180	75.31	74.54
17 „ „ Hydrogen . .	17	7.11	7.34
3 „ „ Nitrogen . .	42	17.58	—
	<hr/> 239	<hr/> 100.00	

#### METOLUIDINE AND BICHLORIDE OF PLATINUM.

Metoluidine is readily soluble in hydrochloric acid. The solution yields, with bichloride of platinum, a dark-yellow precipitate, which is insoluble in water and alcohol, and may be dried at 100°.

On analysis, the following numbers were obtained :

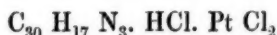
- I. 0.2685 grm. of platinum-salt gave :  
0.3980 „ „ carbonic acid, and  
0.1025 „ „ water.
- II. 0.1897 „ „ platinum-salt gave :  
0.0418 „ „ platinum.
- III. 0.2985 „ „ platinum-salt gave :  
0.0659 „ „ platinum.
- IV. 0.1096 „ „ platinum-salt gave :  
0.0244 „ „ platinum.



These numbers lead to the following percentage-composition :

	I.	II.	III.	IV.
Carbon . .	40·40	—	—	—
Hydrogen . .	4·04	—	—	—
Platinum . .	—	22·03	22·07	22·25

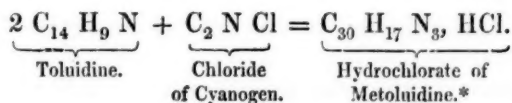
The formula



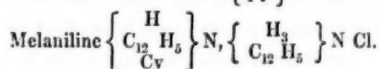
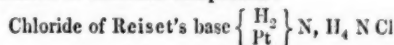
requires the following values :

	Theory.		Experiment.
30 equivs. of Carbon . . .	180·00	40·43	40·40
18 „ „ Hydrogen . .	18·00	4·04	4·24
3 „ „ Nitrogen . .	42·00	9·43	—
3 „ „ Chlorine . .	106·50	20·93	—
1 equiv. „ Platinum . .	98·68	22·17	22·15
1 „ „ Platinum-salt .	445·18	100·00	

The formation of metoluidine is perfectly analogous to that of melaniline; 2 equivalents of toluidine, and 1 equivalent of chloride of cyanogen, yield 1 equivalent of hydrochlorate of metoluidine.



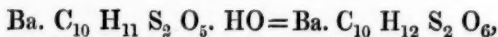
\* The bases produced by the action of chloride of cyanogen upon aniline and toluidine, exhibit a remarkable analogy with one of the platinum alkaloids obtained by M. Reiset, which will at once become perceptible if we compare the formula of the chlorides, when considered as ammonia compounds :



XIX.—*On the Identity of Bisulphamylic and Hyposulphamylic Acids.*

By JOSEPH DANSON, F.C.S.

Owing to the interesting results which have been obtained by Dr. Muspratt\* and Mr. Medlock† with regard to the acids resulting from the action of nitric acid on the sulphocyanides of ethyl, methyl and amyl, and those of Erdmann,‡ Gerathewohl§ and Kopp|| upon acids produced by the action of nitric acid on the bisulphides of the above organic radicals, I have been induced to enter upon the subject with the view of closing the gap which Dr. Muspratt left open in his last paper,¶ *i. e.* proving by analysis the identity of the acid produced by the action of nitric acid on the bisulphide of amyl, with that obtained by Mr. Medlock from the sulphocyanide of amyl. Gerathewohl and Erdmann give for the formula of the baryta-salt of their acid :



differing from Mr. Medlock's formula,  $\text{Ba. C}_{10} \text{H}_{11} \text{S}_2 \text{O}_6$ , by 1 equivalent of hydrogen.

## PREPARATION OF BISULPHIDE OF AMYL.

The preparation of the bisulphide of amyl is analogous to that of the bisulphides of ethyl and methyl. One part of dry sulphamylate of lime, intimately mixed with one part of bisulphide of potassium was introduced into a retort capable of containing three times the quantity of mixture. On the application of heat, some water and a small quantity of a colourless oil distilled; and as the temperature increased, a reddish-yellow oil passed over, possessing a strong odour of garlic. The impure oil was washed with distilled water, and afterwards digested with chloride of calcium, in order to remove the last

\* Chem. Soc. Qu. J. I, 44.

† Chem. Soc. Qu. J. I, 368.

‡ J. Pr. Chem. XXXIV, 447.

§ Löwig's Chemie der organischen Verbindungen, II, 487.

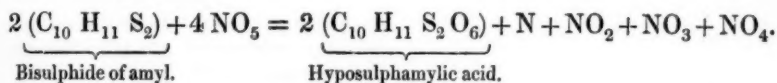
|| Ann. Chem. Pharm. LV, 166.

¶ On the identity of bisulphethylic with hyposulphethylic acid, and of bisulphimethylic with hyposulphamethylic acid. Chem. Soc. Qu. J. III, 18.

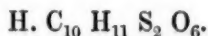
traces of moisture. The anhydrous oil was separated from the chloride of calcium by distilling the mixture in a small retort; the pure bisulphide of amyl passed over as a yellow oil.

#### PREPARATION OF THE ACID FROM BISULPHIDE OF AMYL.

One part of the bisulphide of amyl was placed in a flask immersed in water; one part of nitric acid was added cautiously to it, and agitated occasionally. Under these circumstances, the action goes on very slowly; but if the temperature is slightly increased, the action is very violent, nitrogen, binoxide of nitrogen, nitrous acid and peroxide of nitrogen passing off. The following equation represents the decomposition:



When the disengagement of gas had ceased, the liquid, which was of a green colour, was carefully evaporated over a water-bath till the last trace of nitric acid was expelled, a reddish oily fluid remaining, possessing a most peculiar odour and a strong acid taste. In order to obtain the acid in a state of perfect purity, the fluid was treated with water, in which it readily dissolved, and saturated with carefully prepared carbonate of lead—filtered—and the lead solution decomposed by sulphide of hydrogen; the sulphide of lead was then separated, and the filtrate evaporated on a water-bath to expel all the sulphide of hydrogen. A colourless, oily liquid remained, which is the pure hyposulphamylic acid; The formula resulting from the analysis of the baryta-salt is:



The salts of this acid possess great similarity to those of hyposulphethylic acid, and like them readily crystallize. The potash ammonia, and lime-salts crystallize in colourless plates, easily soluble in water and alcohol. The only salt which I thought necessary to analyse was the baryta-salt.

#### HYPOSULPHAMYLATE OF BARYTA.

When an aqueous solution of the acid is saturated with carbonate of baryta, and then evaporated gently on a water-bath, pearly scales are deposited, which are very soluble in water and alcohol.

## ANALYSIS OF THE SALT.

- I. 0.3800 grms. of salt dried at 100° C. gave :  
     0.3860 „ of carbonic acid and 0.1760 of water.  
 II. 0.1643 „ of salt gave 0.0863 grms. of sulphate of  
         baryta =  
     0.0566 „ of baryta = 34.44 per cent.

## CENTESIMALLY REPRESENTED.

				Found.
				Analysis of the baryta-salt of the acid produced from the sulphocyanide of amyl by the action of nitric acid.
				Analysis of the baryta-salt of the acid produced from the bisulphide of amyl by the action of nitric acid.
				Danson.
		Theory.	Medlock.	Danson.
10 eqs. Carbon	60	27.33	27.46	27.36
11 „ Hydrogen	11	5.01	5.22	5.14
2 „ Sulphur	32	14.58	—	—
5 „ Oxygen	40	18.23	—	—
1 eq. Baryta	76.5	34.85	34.59	34.44
		219.5	100.00	

agreeing with the formula  $\text{BaO} \cdot \text{C}_{10} \cdot \text{H}_{11} \text{S}_2 \text{O}_5$ .

On comparing the above results, we will find that there are good grounds for regarding the acid produced by the action of nitric acid on bisulphide of amyl as identical with that produced by the action of nitric acid on the sulphocyanide of amyl. Gerathewohl's formula for the baryta-salt yields theoretically 5.44 per cent of hydrogen, while mine gives 5.01 per cent. Analysis gives 5.14 per cent.

It is very remarkable that one out of the three analyses made by Gerathewohl corresponds with mine, an additional proof of the identity of the acids. In conclusion, I will, for the sake of comparison, give the amount of carbon, hydrogen, and baryta found in the analysis above referred to along with Mr. Medlock's and my own.

	Carbon.	Hydrogen.	Baryta.
Analysis of the baryta-salt produced by the action of nitric acid on the bisul- phide of amyl . . . . .	27·36	5·14	34·44 Danson.
Analysis of the baryta-salt from the same source . . .			
Analysis of the baryta-salt produced from the sulpho- cyanide of amyl by the action of nitric acid . . .	27·46	5·22	34·59 Medlock.

NOTICES  
OF  
PAPERS CONTAINED IN THE FOREIGN JOURNALS.  
BY HENRY WATTS, B.A., F.C.S.

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**On a Mode of Precipitating all the Metals contained in a Liquid by one Operation  
(in Chemico-legal Investigations).**

**By Gaultier de Claubry.\***

THIS method consists essentially of two parts, viz.: 1. The destruction of the organic matters by the action of nitro-hydrochloric acid; 2. The precipitation of the metals from the resulting solution by electrolytic action.

The organic matter suspected to contain poison, is introduced into strong fuming hydrochloric acid, contained either in a flask, or in a tubulated retort having a receiver adapted to it; a gentle heat is then applied, and nitric acid added by small portions at a time. The organic matter is thereby completely destroyed, with the exception of the fatty substances contained in it. The liquid, which is transparent and colourless, is then decanted off from the fatty matters; the latter are washed several times with distilled water, and melted at each washing; and the several washings added to the main bulk of the liquid. This process is applicable to all descriptions of matter that can become the subject of toxicological investigations: the stomach, intestines, liver, vomited and excrementitious matters, blood, urine, wine, milk, the earth of grave-yards, &c., all yield to it with the utmost readiness; it is much more expeditious than the ordinary process of incineration with sulphuric acid, and less likely to occasion loss. If arsenic is suspected in the matter under examination, the process must be performed with a retort and a receiver, as above described, and the liquid which passes over added to the rest; because chloride of arsenic, being volatile, might otherwise be lost by evaporation; but if the operator is sure of the absence of arsenic, the digestion may be performed in a flask.

A clear solution having been thus obtained, it is concentrated by slow evaporation—to a certain point, easily determined by experience

\* J. Pharm. [3] XVII, 125.



—in order to drive off the excess of acid. It is then introduced into the circuit of a *constant* battery (Bunsen's, for example), the poles being formed of platinum, or the negative pole of platinum and the positive of zinc, if that metal is not to be sought for in the liquid. After a certain time which, even under the most unfavourable circumstances, never exceeds eight or nine hours, the negative pole becomes covered with a crust of the metal or metals contained in the solution. It must be washed with distilled water by means of the wash-bottle, and then digested in nitric acid. The solution thus obtained may be easily tested for all the suspected metals, such as arsenic, antimony, lead, copper, zinc, &c., the operator not being embarrassed by the presence of a large quantity of liquid.

This process is extremely delicate, serving for the discovery of almost infinitesimal quantities of all the metals except silver, which rarely occurs in cases of poisoning. Even lead, which, in the state of chloride, is difficultly soluble in water, nevertheless dissolves with ease in the excess of aqua-regia. The process has, moreover, the advantage of precipitating all the metals at once, and saves the necessity of making special researches for each or any of them—a mode of proceeding which, from insufficiency of material, is often very difficult, or even impracticable.

The concentrated acid solution obtained as above may likewise be treated with sulphuretted hydrogen (after expelling the nitric acid by boiling with excess of hydrochloric acid), or by Marsh's process for the detection of arsenic.

It is sometimes advantageous to make a preliminary trial by digesting the suspected matters in water or alcohol, in which many of the poisons are soluble. If this method be applied, and it is afterwards found necessary to pursue that above-described, we have only to add the aqueous or alcoholic liquor to the said solution, and proceed as before.

The same process may likewise be advantageously applied in the examination of adulterations of food. Bread, for example, is sometimes adulterated with small portions of sulphate of copper. Now the treatment with aqua-regia enables the chemist to operate with facility and expedition on large quantities of bread, whereas the usual method of incineration would be excessively tedious.

The most scrupulous care must, of course, be taken to ensure the purity of the reagents.

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## On the Supersaturation of Saline Solutions.

By H. Löwel.\*

I. Sulphate of soda is much more soluble in hot than in cold water; hence, when a boiling saturated solution of this salt is left to cool in an open vessel exposed to the air, a large quantity of beautiful transparent crystals are deposited, containing 10 equivalents of water of crystallization. Under certain circumstances, however, when a solution saturated at the boiling temperature is cooled in a vessel hermetically sealed, it does not deposit crystals on cooling down to the temperature of the air; the water then retains a larger quantity of the salt than it would be capable of dissolving at the same temperature: it may, therefore, be said to be *supersaturated*. A solution thus supersaturated crystallizes as soon as it is brought in contact with the air; but Gay-Lussac has shown† that this effect is not due to atmospheric pressure. The experiments of M. Löwel are directed to the further investigation of this phenomenon.

II. Three hot solutions of sulphate of soda were formed; each containing 30 grm. of the sulphate and 15 grm. water, and enclosed in glass tubes hermetically sealed. The first tube contained nothing but the solution; into the second were likewise introduced some sharp-edged fragments of glass; and some pieces of platinum were put into the third. For two months, during which the tubes were exposed to temperatures varying from 15° to 25° C. (59° to 87° F.), no crystals were deposited, even on agitation; but when the temperature fell to 6° or 7° C. (43° or 45° F.), crystals were formed in considerable quantity in all the three tubes. The quantity of these crystals showed that the mother-liquids were still in a state of saturation: they did not increase by agitation. When the temperature of the air rose, agitation caused the crystals to disappear, but they separated out again, when the temperature fell to 7° or 8° C.

On breaking the tubes, and decanting the mother-liquids into capsules, the two following phenomena were observed:—1. The crystals in the tubes, when touched with a glass rod, became opaque throughout their whole mass, the opacity beginning at the part touched by the rod; the same effect was produced after a while by mere contact of air. 2. The mother-liquids decanted into the capsules solidified in crystalline masses. The crystals in the tubes were sulphate of soda, containing 8, or perhaps only 7, atoms of water. This salt has been noticed by Faraday and Ziz. The crystals derived from the mother-liquids on exposure to the air were ordinary sulphate of soda containing 10 atoms of water.

III. M. Löwel has made numerous observations on the preparation of sulphate of soda with 8 atoms of water. This salt crystallizes

\* Compt. Rend. XXX, 163; also Ann. Ch. Phys. [3] XXIX, 62.

† Ann. Ch. Phys. [2] II, 256.

in long prisms, with rhombic bases; it becomes opaque when touched by certain bodies, and this effect is attended with evolution of heat. The mother-liquid of these crystals retains, at a given temperature, a definite quantity of the eight-atom sulphate.

It has hitherto been supposed that the state of supersaturation of saline solutions is very instable, inasmuch as it appears to be destroyed by causes purely mechanical, such as agitation, or the contact of a solid body which, chemically speaking, is quite inert. But the preceding experiments show that neither agitation of the liquid nor the introduction of fragments of glass or platinum wire into the supersaturated solution before cooling, has any influence on the formation of crystals. The electric current produces no alteration in a solution of sulphate of soda with 8 atoms of water. A solution of this salt evolves heat in crystallizing, as observed by Gay-Lussac; and the crystallized sulphate, as already mentioned, likewise becomes heated in passing from the transparent to the opaque condition.

IV. A boiling saturated solution of sulphate of soda poured into a capsule exposed to the air, becomes covered with a pellicle of anhydrous salt, and between  $32^{\circ}$  and  $29^{\circ}$  C. ( $90^{\circ}$  and  $84^{\circ}$  F.) yields crystals containing 10 atoms of water, the pellicle gradually disappearing. If the capsule into which the boiling solution is poured be placed under a bell-jar, so that the air in contact with it is but slowly renewed (*e. g.* a jar of the capacity of 6 or 8 litres for a capsule containing 1 litre of solution), the liquid will retain its state of supersaturation during cooling, and no crystals will be formed till the temperature falls below  $12^{\circ}$ , when crystals containing eight atoms of water will be deposited.

The solution may continue supersaturated for a week or a fortnight, neither sudden jerks, nor vibrations, nor agitation giving rise to any formation of crystals; but if the bell-jar be removed, the liquid solidifies in a mass, consisting of crystals containing 10 atoms of water. If quick-lime be placed under the jar, the temperature being  $24^{\circ}$  C. ( $75^{\circ}$  F.), the solution yields crystals containing 8 atoms of water.

If a flask in which boiling water has been saturated with sulphate of soda be covered with a small capsule of glass or porcelain, the liquid will remain in the state of supersaturation. In open tubes, of 6 to 10 millimetres diameter, the state of supersaturation continues for a very long time—that is to say, for four, six, or eight weeks, or even longer. Crystallization always commences at that part of the liquid which is in contact with the air.

V. Agitation does not bring about the crystallization of the sulphate containing 10 atoms of water; but the introduction of a crystal of the salt, or the mere contact of a rod of glass or metal determines it.

M. Löwel has made some very interesting observations on the

circumstances of *contact* which may or may not induce the crystallization of the ten-atom salt. A rod of glass or metal, which determines the formation of the ten-atom sulphate when plunged into the supersaturated solution, loses this property if it has been previously heated to between  $40^{\circ}$  and  $100^{\circ}$  C. If this were not the case, why should a supersaturated solution placed in a basin under a bell-jar, remain unaltered till the temperature falls to  $8^{\circ}$  C.?

A rod of glass or metal, previously heated to  $100^{\circ}$  C., preserves its property of not inducing crystallization, even for ten days or a fortnight, the temperature varying from  $0^{\circ}$  to  $20^{\circ}$  C., provided that the rod be fitted into a cork, and the cork inserted into the mouth of a bottle filled with air, so that the greater part of the rod may be preserved from free contact with the air; for, if the rod be taken out of the bottle and exposed to the air for a quarter of an hour, it will afterwards determine the crystallization of the solution. It appears then that rods of glass or metal lose their activity when heated, but recover it by contact with the open air. The rods also lose their activity by contact for twelve hours with water, but recover it when dried by free exposure to the air.

Water does not induce the crystallization of the supersaturated solution. Cold alcohol determines it; hot alcohol does not.

VI. M. Löwel has succeeded in forming supersaturated solutions by dissolving sulphate of soda at temperatures not exceeding  $26^{\circ}$  C. ( $79^{\circ}$  F.) He has likewise shown that a supersaturated solution of sulphate of soda, concentrated by evaporation in a glass vessel previously deprived of its activity, yields crystals of the salt containing 8 atoms of water.

It would appear, says M. Löwel, that those bodies which determine the crystallization of the ten-atom sulphate *attract* the crystalline molecules, while passive substances *repel* them. This seems to indicate that the sides of vessels containing a supersaturated solution exert an action opposed to that of the air.

VII. In fact, without the action of the air, and of those bodies which determine the crystallization of the ten-atom sulphate, we should not have been acquainted with any sulphate containing more than 8, or perhaps 7, atoms of water. The latter proportion M. Löwel considers more probable than the former.

VIII. Similar phenomena are exhibited by carbonate of soda, common alum, chrome-alum, &c.

## On the Nitride of Boron.

By F. Wöhler.

Balmain,\* as is well known, discovered about eight years ago a compound of boron and nitrogen, to which, on account of its alleged property of combining, like cyanogen, with metals, he gave the analogous name, *Æthogen*.† At a later period, he found that all the bodies which he had described as æthonides were one and the same substance, namely, nitride of boron, containing an unessential amount of metal.‡ He obtained this compound by heating boracic acid, either with cyanide of potassium, or cyanide of zinc, or with sulphur and cyanide of mercury. I have subsequently found that it may be advantageously prepared by igniting an anhydrous mixture of borax and ferrocyanide of potassium.§

The observation that nitride of tungsten|| is formed when tungstate of potash is heated with sal-ammoniac, led me to attempt the formation of nitride of boron in a similar manner. This experiment has fully realized my expectation. I obtained a body possessing all the properties of the compound prepared by Balmain by means of the cyanides, and consisting, as I shall show further on, of boron and nitrogen, in such proportions as to be converted, by the action of water, into boracic acid and ammonia.

For the preparation of nitride of boron according to this method, one part of pure and perfectly anhydrous borax is intimately mixed with two parts of dried sal-ammoniac; the mixture transferred to a porcelain, or better, to a platinum crucible; the crucible covered, and the whole exposed to a full red heat. An ordinary earthen crucible is less suited for the purpose, since the product is likely to become contaminated with iron, in consequence of the formation of sesquichloride. In the preparation of smaller quantities, a glass vessel may be employed. By this method, a white, infusible, porous mass is obtained, which is to be finely pulverized and heated to perfect ebullition in a large quantity of water, to which some hydrochloric acid has been added.¶ The nitride of boron is then deposited as a white powder, which is separated by filtration, well washed with hot water, and finally dried.

When prepared with earthen crucibles, or with impure borax

\* Chem. Soc. Mem. Vol. I, p. 149, and Vol. II, p. 15.

† J. Pr. Chem. B. XXVII, S. 422, and B. XXX, S. 14.

‡ J. Pr. chem. XXXII, 494.

§ Berzelius, Lehrbuch III, 113.

¶ Nachrichten 1850, N. III, S. 33.

¶ If, in the first place, pure water be employed and the filtered solution slowly evaporated, chloride of sodium separates in acute and transparent octohedrons. These crystals, when heated, become milk-white, without losing either their form or their lustre. From their solution in water the salt is again obtained in cubes.



which has not been recrystallized, it must be digested with concentrated hydrochloric acid, for the purpose of removing foreign matters; but even by this process it is difficult to obtain it in a state of purity.

When thus prepared, the nitride of boron forms a white, light powder, which, when magnified 500 times, appears as an amorphous, granular, milk-white mass. It may be rubbed into the skin, like talc, and imparts to it a high degree of smoothness. It possesses all the characteristic properties assigned to it by Balmain; becomes luminous in the edge of a flame, giving off a greenish-white light; evolves ammonia in abundance, when fused with hydrate of potash; suffers no change either with concentrated acids or with alkalis; and is not affected by ignition in hydrogen or chlorine. In a current of steam, it is completely converted, even at a moderate red-heat, into ammonia and boracic acid, the latter being for the most part volatilized with the aqueous vapours; a solution of borate of ammonia is obtained on their condensation.

I have, moreover, made the following observations upon this substance.

Exposed for an hour to a temperature at which nickel fuses, in a porcelain crucible, which was placed in an earthen crucible and surrounded by pulverized charcoal, nitride of boron remained entirely unchanged, neither fusing nor suffering any loss of nitrogen.

In an alcohol-flame into which a jet of oxygen is blown, it rapidly burns with a greenish-white flame, forming vapours of boracic acid. On the contrary, it cannot be made to burn by directing a jet of oxygen upon it whilst heated to full redness in a small platinum crucible; nor does it even become luminous under these circumstances. Its most remarkable property of phosphorescing with a greenish-white light of greater brilliancy than is exhibited by any other body, is perceptible only if it be ignited in contact with a flame, and is invariably attended with slow oxidation. When heated in chlorine, it appeared to possess this property in a higher degree, but seemed to lose it altogether by the presence of foreign matters.

Nitride of boron is, moreover, distinguished by the property of forming binoxide of nitrogen and nitrous acid when heated with easily reducible metallic oxides; in this case a reduction of the oxides takes place, but without incandescence. When it is heated in a glass tube with protoxide of lead, copper, or mercury, the tube becomes filled with dense red vapours. Heated with water in a sealed glass tube to  $200^{\circ}$ , nitride of boron reproduces ammonia and boracic acid: the conversion, however, at this temperature is effected but very slowly. When the action is allowed to continue many hours, the glass of the tube, if the substance has not exploded, is found to be attacked to a considerable depth, and converted into a white substance



resembling opal; the water, on examination, is then found to contain potash, silicic acid and boracic acid, together with free ammonia.

Although even hot concentrated sulphuric acid is without action upon nitride of boron when allowed to remain in contact with it only for a short time, it nevertheless converts the nitride, though very slowly, into boracic acid and ammonia, when heated with it to a temperature at which the acid evaporates. This change is more readily effected by digesting with fuming hydrochloric acid, whereupon borofluoride of ammonium is formed.

Nitride of boron exhibits the most remarkable deportment when heated with anhydrous carbonate of potash; it thus becomes converted into boracic acid and cyanate of potash, the carbonic acid being reduced to the state of carbon, which, uniting with the nitrogen, gives rise to the formation of cyanogen. This is, indeed, an unexpected method of producing this radical, although it is in perfect accordance with Berzelius's observation, that free boron, when heated with carbonate of potash, burns at the expense of the carbonic acid, and liberates carbon. One equivalent of nitride of boron and 2 equivalents of carbonate of potash [ $\text{BN} + 2(\text{KO} \cdot \text{CO}_2)$ ] contain the elements of 1 equivalent of borate and 1 equivalent of cyanate of potash ( $\text{KO} \cdot \text{BO}_3 + \text{KO} \cdot \text{C}_2\text{NO}$ ). This double decomposition may be very readily effected, even at a gentle red-heat, in a platinum crucible, placed over a large spirit-flame. A mixture of nitride of boron and dry carbonate of potash in the above equivalent proportions (1 : 3 by weight), fuses readily and quietly to a pellucid liquid at a temperature at which carbonate of soda alone is not liquefied. On cooling, it congeals to a highly crystalline white mass, which consists nearly of equal parts, by weight, of borate and cyanate of potash, being perfectly soluble in water. I have converted it into pure and beautifully crystallized urea, from which I have prepared cyanuric acid in the crystalline form. If nitride of boron be employed in excess, a portion of cyanide of potassium is simultaneously formed, from which I was enabled to prepare prussian-blue and hydrocyanic acid. Nitride of boron, even when strongly heated in a porcelain tube with free carbonic acid, occasions no decomposition of this gas.

As far as the direct proofs of the composition of nitride of boron are concerned, the analyses, when made with specimens of different preparation, exhibited considerable discrepancies. It was evident that this body, unless prepared with every possible care, is liable to great variations of composition, being obstinately combined with a foreign admixture, which appears chiefly to consist of boracic acid. I will not quote these experiments, but will adduce only some closely concordant analyses performed with substances which had been carefully prepared in different operations.

Owing to the facility with which nitride of boron evolves ammonia

when in contact with hydrates, no difficulty was experienced in determining the amount of nitrogen. The determination was made exactly as with an organic substance, namely, by igniting with soda-lime containing somewhat more hydrate of soda than usual, in order to render it more fusible. Four analyses with substances of different preparations, all of which were made by Dr. Städler, gave 48.13, 49.63, 50.77, and 51.36 per cent of nitrogen. The nitride of boron employed in the last analysis, which yielded 51.36 per cent of nitrogen, had been treated with hydrofluoric acid.

0.289 grm. gave 2.363 grm. of bichloride of platinum and ammonium.

For the direct determination of the amount of boron, there remained only one method, namely, oxidation by heating with an accurately weighed quantity of nitrate of lead. The increase in the weight of the fused residue beyond that of the residual oxide of lead could only be boracic acid.

This method, which may likewise be employed in many other cases, is very readily and quickly executed, and appears to give very accurate results. For this purpose, the salt must of course be perfectly pure, and very finely pulverized. As it is decomposed even at a moderate heat, it is necessary to dry it with great care. The fusion may be effected in a platinum-crucible, provided a large excess of the salt be employed; but if too small a quantity be taken, a portion of lead is reduced, and becomes alloyed with the platinum.

The mixing of the substance to be oxidized with the salt, is performed in the crucible by means of a thick polished platinum wire, the two bodies being very intimately incorporated. As the mass intumescs somewhat strongly, it is necessary to heat it at first very carefully. It is afterwards heated to redness for some seconds, till the mass flows quietly.

0.180 grm. of nitride of boron, which had been treated with hydrofluoric acid, and dried at  $150^{\circ}$ , gave, when fused with 6.068 grms. of nitrate of lead, 4.334 grms. of fused residue. By deducting the quantity of protoxide of lead contained in the salt used, (which amounted to 4.088 grms.), there remained 0.246, representing the boracic acid which had been formed. The latter contained 0.0763 grm. of boron, or 42.66 per cent in the nitride of boron. A second experiment yielded 42.23 per cent.

Five other experiments with nitride of boron obtained in three different preparations gave 41.93, 41.61, 40.88, 40.87, 40.38 per cent of boron. If we assume the highest numbers found for boron and nitrogen as the most correct, we obtain in 100 parts:

Boron	.	.	42.66
Nitrogen	.	.	51.36
Loss	.	.	5.98

This loss can be nothing but oxygen, which probably exists in the compound in the form of boracic acid; for the nitride, as special experiments have shown, contains neither chlorine nor sodium. Calculated in equivalents, the above composition would represent a compound of 1 equivalent of boracic acid with 14 equivalents of nitride of boron ( $\text{BO}_3 + 14 \text{BN}$ ), which would contain:

Boron	.	.	42.617
Nitrogen	.	.	51.124
Oxygen	.	.	6.259

A compound of this nature, however, is highly improbable. It may be assumed with far greater probability, that the amount of boracic acid, which varies considerably, remains mechanically mixed, in consequence of the mode of formation and of the entirely unfused, amorphous condition of the nitride of boron; in a similar manner, for instance, as sugar, if mixed with boracic acid and carbonized, would yield a carbon, from which it would probably be difficult to extract the entire quantity of boracic acid by means of solvents.

Pure nitride of boron  $\text{BN}$ , free from boracic acid, has not yet been prepared,—unless Balmain's product, which has not hitherto been analysed, should be found to be the pure substance.

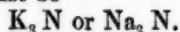
It would contain:

Boron	.	.	43.76
Nitrogen	.	.	56.24

#### On the Amido-nitrides of Tungsten.

By F. Wöhler.\*

Gay-Lussac and Thénard have shown† that potassium and sodium, under the influence of heat, absorb ammonia with evolution of hydrogen, giving rise to compounds of a dark-green colour; these compounds have been distinguished by the names of *Ammonio-nitride of Potassium* and *Ammonio-nitride of Sodium*. The hydrogen disengaged during the reaction corresponds to half the volume of ammonia absorbed. In presence of water, these compounds are resolved into an alkaline hydrate and ammonia. When heated, they are transformed into ammoniacal gas and a nitride, which, in contact with water, gives rise to an alkaline hydrate and ammonia; hence the composition of the nitride must be

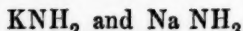


From these facts it may be concluded—in accordance with the

\* Ann. Pharm. LXXIII. 190; Ann. Ch. Phys. [3] XXIX, 187.

† Recherches Physico-chimiques I, 337.

opinions of Berzelius\* and of L. Gmelin†—that the green substances obtained by Gay-Lussac and Thénard are compounds represented by the formulæ



These properties of the alkali-metals may serve to throw some light on the nature of certain compounds which are formed by the action of ammoniacal gas on tungstic acid or chloride of tungsten raised to a certain temperature.

When bichloride of tungsten is subjected to the action of ammoniacal gas, a substance is obtained composed of nitride and amide of tungsten, which may, therefore, be called *Amido-nitride of Tungsten*. The chloride of tungsten used in this preparation was obtained by burning metallic tungsten in chlorine gas free from atmospheric air. It was then rapidly introduced into a long and perfectly dry glass tube, and a current of ammoniacal gas passed over it, the tube being shaken from time to time. It is not necessary to apply heat at the commencement of the operation, as the action of the ammonia on the chloride of tungsten develops sufficient heat to fuse part of the sal-ammoniac formed and volatilize the rest, which then condenses on the surface of the chloride. Towards the end of the operation, however, the application of heat from without is necessary, care being taken not to exceed the temperature at which the sal-ammoniac sublimes. As soon as all the chlorine is converted into sal-ammoniac and no more of that compound is formed, the tube is allowed to cool, the current of ammoniacal gas being kept up all the while.

The product of this operation is a black substance, exhibiting traces of fusion here and there—an effect which arises from the chloride of tungsten having been partly melted by the heat produced during the reaction. In this state it is denser, and has a kind of metallic lustre, resembling that of the graphite from gas-retorts. When heated in the air, it first gives off ammonia, then takes fire, and is converted into tungstic acid. Heated in a porcelain crucible to a temperature near the melting-point of silver, it loses its nitrogen and hydrogen, and is reduced to the state of metallic tungsten. It likewise behaves in the same manner when heated to low redness in a current of hydrogen; in this case, a large quantity of ammonia is given off. By fusion with hydrate of potash, it is converted into tungstate of potash, giving off ammonia and hydrogen. It is not acted upon by alkalis in the state of aqueous solution, or by acids; it retains with energy a certain quantity of chloride of tungsten, or of sal-ammoniac, and must, therefore, be purified by digestion, first in

\* Lehrbuch der Chemie, 5 Ausg. II, 71.

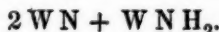
† Hand-book of Chemistry (translation) III, 66.

potash-ley and then in ammonia, and afterwards washed with water, before it can be considered sufficiently pure for analysis.

The tungsten of this compound was estimated either as tungstic acid or as metallic tungsten. The quantities obtained in different experiments varied between 86.76 and 90.8 per cent, according to which results, the sum of the nitrogen and hydrogen varies between 13.24 and 9.2 per cent. The specimen which contained 90.8 per cent of tungsten yielded 8.26 per cent of nitrogen, by Will and Varrentrapp's method.

From these results it would appear that there exist two amido-nitrides of tungsten; and, in fact, the compound prepared by the process above-described, gives off ammonia with the greatest facility when heated, and is transformed into a compound richer in tungsten; hence it is probable that a portion of this latter compound is formed during the preparation of the former.

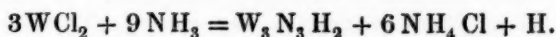
The compound formed directly by the preceding process is composed of



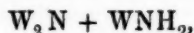
It contains

		Calculated.		Found.
3 W . . .	285	—	86.61	86.76
3 N . . .	42	12.79	13.39	{ 13.24
2 H . . .	2	0.60		
	329		100.00	100.00

Its formation may be represented by the equation



On heating this compound in a current of hydrogen, it gives off 1 equivalent of nitrogen, which is evolved in the form of ammonia, and leaves a residue consisting of the second amido-nitride,



which is distinguished by the grey colour of its powder. This substance contains:

		Calculated.		Found.
3 W . . .	285	90.48		90.80
2 N . . .	28	8.89		8.24
2 H . . .	2	0.63		—
	315	100.00		

It is formed on heating the first compound, mixtures of the two being however produced, which vary with the temperature. Both

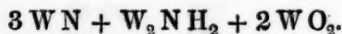
these amido-nitrides, when strongly heated, are reduced to the metallic state.

*Oxyamido-nitride of Tungsten.*— $3 \text{WN} + \text{W}_2\text{N}_2\text{H}_2 + 2 \text{WO}_2$ .—This compound is formed by the action of gaseous ammonia on heated tungstic acid. It is not easily obtained in a state of definite composition; for it readily gives off nitrogen and hydrogen when heated either in the air or in a current of hydrogen.

The tungstic acid used in the preparation of this compound was obtained by calcining crystallized tungstate of ammonia. It was finely pulverized, then spread in a thin layer over the inner surface of a long glass tube, and exposed to a current of ammoniacal gas. Heat was applied till a faint incandescence showed itself, the tube being frequently turned. The operation was complete when the evolution of water ceased. In the course of the process, the decomposing action which the compound exerts on gaseous ammonia becomes apparent. If the tungstic acid were placed in a porcelain tube, and the temperature raised to the melting-point of silver, nothing but metallic tungsten, or a mixture of the metal and the oxyamido-nitride, would be obtained.

This compound is of a pure black colour. When prepared with non-pulverized tungstic acid—*e. g.*, in the state in which it is obtained by calcining tungstate of ammonia—it forms black scales, having a semi-metallic lustre. When heated it gives off ammonia. It resists the action of acids and alkalis; but if the action of the ammonia on the tungstic acid has not been exhausted, potash in the state of aqueous solution disengages a small quantity of ammonia from the compound, and abstracts a corresponding quantity of tungstic acid. Hypochlorite of soda decomposes the compound, nitrogen being evolved, accompanied by an odour of chloride of nitrogen, and tungstate of soda formed. Oxyamido-nitride of tungsten burns brilliantly when heated in the air, and is converted into tungstic acid. Like metallic tungsten and tungstic oxide, it burns when heated with red lead or oxide of copper. It is completely reduced to the metallic state by ignition in a current of hydrogen, water and ammonia being evolved. When heated with water in a sealed tube, it supports without alteration a temperature of  $230^\circ \text{C}$ .

This compound gave by analysis results nearly corresponding to the formula



Its composition in 100 parts is as follows:

	Calculated.	Found.
Tungsten . . . . .	88.04	88.03
Nitrogen . . . . .	7.44	7.15
Hydrogen . . . . .	0.27	0.20
Oxygen . . . . .	4.25	4.64



The mutual decomposition of tungstic acid and ammonia appears then to be less simple than might be supposed from considering merely the composition of these substances; for it might have been supposed that 1 equivalent of tungstic acid and 1 equivalent of ammonia would produce 3 equivalents of water and 1 equivalent of nitride of tungsten,  $W N$ , containing 87.11 per cent of the metal, a quantity nearly the same as that contained in the oxyamido-nitride.

The latter compound, or, at least, a substance analogous to it, may be obtained by fusing, at a high temperature in a platinum crucible, a mixture of tungstate of potash with a large excess of sal-ammoniac, the whole being covered with a layer of chloride of potassium. If the fused product be afterwards treated with water, and the tungstic acid removed by means of weak potash-ley, a black, heavy residue is obtained, which is the new compound. When examined by a microscope with a magnifying power of 100, it is found to consist of black metallic molecules. It is this substance which Wöhler, six-and-twenty years ago, erroneously described under the name of black oxide of tungsten.\* It contains nitrogen and hydrogen, and gives off a large quantity of ammonia, not only by contact with alkalis, but even when simply heated by itself. The presence of the hydrogen in a compound formed at so high a temperature is difficult to account for, unless it be admitted that this hydrogen does not enter into the molecule till water is introduced. Another curious fact is, that this substance, when heated to whiteness in a close vessel, yields metallic tungsten. For the rest, this body exhibits the same characters as that which is obtained by the direct action of ammoniacal gas. It yielded between 88 and 89 per cent of tungsten; but when decomposed by a current of chlorine, which caused it to volatilize in the state of chloride and of acid chloride, it likewise left a residue of potash, amounting to between 1 and 2 per cent.

When a mixture of tungstate of soda and sal-ammoniac is fused beneath a layer of chloride of sodium, and afterwards treated with water and dilute solution of potash, a dark-brown substance is obtained, which, when examined by the microscope, is seen to consist of a black and a dark copper-coloured substance. Wöhler is of opinion that the latter is the tungstate of tungstic oxide and soda which he described some time ago.

Brown oxide of tungsten, slightly calcined in a current of ammoniacal gas, likewise yields a hydrogenized and azotized body, mixed, however, with unaltered oxide, which may be easily recognized by its dark-brown colour. When strongly ignited in a porcelain tube, it leaves the pure metal.

Berzelius states that tungstic oxide is reduced to the metallic state by strong ignition in a current of hydrogen. According to

\* Pogg. Ann. II, 347.

Wöhler's observations, on the contrary, tungstic acid is reduced to the state of tungstic oxide when heated in an atmosphere of hydrogen to the melting-point of silver, but the oxide undergoes no further change. The observations of Berzelius probably applies to an oxide containing a small quantity of alkali. Tungstic oxide, when very pure, has a fine brown colour inclining to violet. Under the microscope it has a metallic aspect, very much like that of gun-metal; it appears to be slightly fretted or crystalline.

Wöhler has not succeeded in obtaining a nitride of tungsten free from hydrogen. On calcining tungstic acid in cyanogen gas, a black substance, having a metallic aspect, was obtained, and a considerable quantity of carbonic oxide. The black substance, when treated with potash, yielded a little ammonia; nitrogen, therefore, enters into its constitution, but it likewise contains carbon. The amount of tungsten contained in it was 64.5 per cent.

On the Action of Ammonia on Chloroplatinate of Ammonium.

By C. Gerhardt and A. Laurent.\*

It is known that chloroplatinate of ammonium, when digested with concentrated ammonia, dissolves completely without colouring the liquid. This product has been examined by Laurent and Gerhardt. Alcohol throws down from it an abundance of white flakes, which, on drying, are converted into a pale-yellow resinous mass, easily soluble in water. The alcoholic liquid contains a large quantity of ammonia; and even the dried resin must be re-dissolved in boiling alcohol, because it always retains a considerable quantity of sal-ammoniac.

The resin dried at 160° C. gave by analysis results nearly corresponding to the formula,  $\text{Pt Cl N}_2 \text{H}_5$ .

	Calculated.		Found.		
Pt . . .	99.0	59.1	57.9	57.4	58.2
Cl . . .	35.5	21.2	22.4	—	20.4
N <sub>2</sub> . . .	28.0	16.7	15.0	—	—
H <sub>5</sub> . . .	5.0	3.0	3.1	—	—
	<u>167.5</u>	<u>100.0</u>	<u>98.4</u>		

The substance analysed was not absolutely pure; for when heated to 160° — 210° C., it gave off traces of water and ammonia, and, when more strongly heated, evolved hydrochloric acid, and became insoluble. The impossibility of obtaining the substance in regular

\* Compt. Rend. Trav. Chim. 1849, 113; Ann. Ch. Pharm. LXXII, 223.

form precluded the more accurate investigation of this circumstance. It was, however, ascertained that the body forms white precipitates with oxalate, sulphate, and carbonate of ammonia; these precipitates, however, refused to crystallize, and yielded variable results on analysis. The precipitate formed by carbonate of ammonia gives off carbonic acid when brought in contact with acids. Nitrate of silver added to the solution of the resin forms a precipitate which appears to be a mixture of chloride of silver, and another platinum-salt insoluble in water.

Whatever may be the composition of these precipitates, it may be safely concluded that the resin is the chloride of a platinum-base, analogous to those discovered by Gros and Reiset.

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On the Cyanogen-compounds of Titanium.

By F. Wöhler.

I. *Chloride of Cyanogen and Titanium*.<sup>\*</sup>— $\text{Cy Cl} + 2 \text{Ti Cl}_2$ .—In the memoir on titanium contained in this Journal, vol. II, p. 352, the author states that chloride of cyanogen and chloride of titanium combine in definite proportions. Had it not been for the existence of this compound, it is probable that the copper-coloured cubic crystals of titanium would still for a long time have been regarded as the pure metal; for it was this compound which, by its volatility and tendency to form a crystalline substance, betrayed the existence of cyanogen in the copper-coloured crystals. The investigation of its composition was, therefore, a matter of some interest.

The compound is formed immediately, and with great rise of temperature, when gaseous chloride of cyanogen is brought in contact with chloride of titanium.† In a short time, the latter is converted into a bulky, yellow, crystalline mass, which must be gently heated and repeatedly agitated, in order to saturate it completely with chloride of cyanogen.

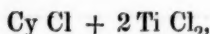
The chloride of cyanogen and titanium is lemon-yellow and very volatile. At a temperature considerably below  $100^\circ$ , it begins to

<sup>\*</sup> Ann. Ch. Pharm. LXXIII, 219.

† The chloride of cyanogen is most easily prepared as follows:—A saturated solution of cyanide of mercury, into which an excess of finely pounded cyanide has been sifted, is saturated with chlorine gas, and the upper part of the containing-vessel above the liquid likewise filled with the gas. The vessel is then closed, and left in a dark place, till, after repeated agitation, the whole of the chlorine is absorbed, or the whole of the cyanide of mercury dissolved. Any free chlorine which remains may be removed by agitating the liquid with metallic mercury. The solution is then poured into a flask, the flask connected with a chloride-of-calcium tube, and the latter with a gas-delivery tube, and heat applied till the liquid enters into gentle ebullition from the escape of chloride of cyanogen. If it be desired to obtain the chloride of cyanogen in the free state, either liquid or crystallized, the object may be attained by passing the gas into a tube surrounded with snow and salt.

volatilize, and sublimes in transparent, lemon-yellow crystals, which appear to be rhombic octohedrons. In damp air it fumes very strongly, and soon becomes milk-white, emitting at the same time the pungent odour of chloride of cyanogen. Water dissolves it with great rise of temperature and evolution of gaseous chloride of cyanogen, forming a perfectly clear solution. It dissolves without alteration in heated chloride of titanium, and separates again in crystals on cooling. It absorbs ammoniacal gas, with great evolution of heat; forming a deep orange-red compound, which likewise turns white in damp air, and is decomposed by water with partial separation of titanio acid.

The composition of chloride of cyanogen and titanium is expressed by the formula :



which gives in 100 parts :

Chloride of cyanogen . . . . .	24.44
Chloride of titanium . . . . .	75.56
	<hr/>
	100.00

To analyse the compound, an indefinite quantity of chloride of titanium was introduced into a weighed bulb-apparatus; spread in a thin layer over the inner surface; then completely saturated with chloride of cyanogen; and the product weighed after all excess of chloride of cyanogen had been removed by a current of dry air. The compound was then carefully dissolved in water, and the titanio acid precipitated at a boiling heat by aqueous ammonia. In this manner, 3.008 grm. of the compound yielded 0.964 grm. titanio acid, corresponding to 2.283 grm., or 75.89 per cent of chloride of titanium.

Bichloride of tin does not appear to form any similar compound with chloride of cyanogen.

II. *Compound of Bichloride of Titanium with Hydrocyanic acid.\**— $\text{H Cy} + \text{Ti Cl}_2$ .—When anhydrous hydrocyanic acid is poured upon bichloride of titanium, combination takes place instantly, with rise of temperature and ebullition, and the two liquids are converted into a pulverulent, yellow mass. On account of the violence of the action, it is advisable either to cool the liquids to  $0^\circ \text{C}$ . before mixing, or to conduct the hydrocyanic acid in the gaseous form into the liquid chloride of titanium contained in a tubulated retort. When the saturation is complete, the excess of hydrocyanic acid is distilled off at a gentle heat, and the compound sublimed into the neck of the retort by the application of a gentle heat, in order to purify it from any titanio acid with which it may be mixed.

This compound is very volatile, and begins to sublime at a tem-

\* Ann. Ch. Pharm. LXXIII, 226.

perature below  $100^{\circ}$ . It then condenses in transparent, lustrous, lemon-yellow crystals, very much like those of the chloride of cyanogen and titanium, even in their form, which is that of a rhombic octohedron, sometimes simple, sometimes combined with other forms. The compound does not fuse before volatilizing; but yet the crystals, when quickly sublimed, generally unite into a coherent mass which separates from the glass on cooling. The compound fumes slightly in the air, smells strongly of hydrocyanic acid, soon turns white, and deliquesces to a transparent viscid solution. When passed in the state of vapour through a glass tube heated to low redness, it is decomposed, and covers the glass with copper-coloured nitride of titanium having a darker colour than usual, from separation of carbon. It is not altered by sublimation in chlorine gas, the hydrogen not being separated by that treatment.

This compound appears by analysis to contain 1 equivalent of hydrocyanic acid and 1 equivalent of bichloride of titanium:



whereas the chloride of cyanogen and titanium contains 2 equivalents of bichloride of titanium. According to this formula, it should contain in 100 parts:

Hydrocyanic acid . . . . .	22.14
Bichloride of titanium . . . . .	77.86

3.962 grm. of this compound, weighed in the neck of the retort in which it had sublimed—the neck having been melted off for the purpose—then dissolved in water, and precipitated with ammonia at a boiling heat, yielded 1.316 grm. of ignited titanac acid, corresponding to 3.117 grm. or 78.67 per cent of bichloride of titanium. A compound with 2 equivalents of the bichloride would contain 87.55 per cent.

#### On the Physiological Action of Analogously Constituted Chemical Compounds.

By J. Schlossberger\*

A series of experiments on the action of chemically pure *Methyl-alcohol* and *Amyl-alcohol*, made by the author, partly alone, partly in conjunction with Professor Griesinger, on dogs, cats, and rabbits, led to the following results:

I. Both these alcohols exert upon the animal organism an action precisely similar to that of common alcohol (ethyl-alcohol), inasmuch as they uniformly, when administered in comparatively small doses, excite intoxication to a greater or less degree, and in large doses

\* Ann. Ch. Pharm. LXXIII, 212.

produce perfectly comatose sleep. With regard to energy of narcotic action, amyl-alcohol appears scarcely to surpass absolute ethyl- or methyl-alcohol. Large, powerful dogs, bore doses of an ounce of wood-spirit, or half an ounce of fusel-oil, without passing from the state of coma or apparent death, to that of actual death.

II. Both these alcohols, just like ethyl-alcohol, are *very quickly decomposed in the blood*, so that frequently, after the lapse of a few hours, their odour cannot be detected—or at most but slightly—in that fluid, even on distillation. In two cases, however, when the carotid artery was opened, half an hour after the injection of a considerable quantity of fusel-oil into the stomach, a very distinct odour of fusel-oil was perceived in the blood of that vessel; the same was apparent in several instances in the blood of the jugular veins and of the heart. The alcohols are therefore, partially at least, *absorbed from the stomach into the blood without alteration*.

In certain glands, such as the spleen and liver, which contain large quantities of blood, the odour continued very distinct, and for a very long time after the introduction of the alcohol into the stomach. In the brain of animals, on the contrary, into whose system wood-spirit or fusel-oil had been injected by the stomach or the rectum, the odour of these substances was *never* unmistakeably perceptible.

III. *On the mucous membranes*, the above-mentioned anhydrous alcohols act precisely in the same manner as common alcohol, altering the structure of the epithelium, drying it up, making it easily separable, and producing partial reddening, and extravasation of blood on the mucous membrane itself.

IV. The question, whether these alcohols, during their decomposition in the circulating system, are converted into the corresponding acids (*i. e.* undergo eremacausis) before they are completely burned—the author was unable to bring to a satisfactory solution, inasmuch as his experiments gave contradictory results. In two experiments (on dogs), in which wood-spirit was injected into the stomach, and the liquid part of the blood, after the separation of the coagulable portions, was distilled with very dilute sulphuric acid, a distillate was obtained which gave unmistakeable reactions of *formic acid* (with oxide of silver, oxide of mercury, &c.) But in a similar experiment with fusel-oil, *no valerianic acid* could be discovered in the blood, by similar means, although that acid is so easily recognized by its odour. Bouchardat and Sandras believe that they found traces of acetic acid in the blood of animals whose food had been soaked in brandy. With regard to the first-mentioned result (with wood-spirit), it still remains to be decided whether the blood of dogs in its normal state, that is, when the animals are fed on a mixed diet, does not contain traces of formic acid.

The author often observed that the liver and spleen of animals which had taken considerable quantities of fusel-oil, from one to four



hours before death, gave out a pure and distinct odour of valerianic acid, after they had lain exposed to the air for several days, although during dissection they merely smelt of fusel-oil. The odour of valerianic acid became apparent before the commencement of putrefaction; moreover, from causes which the author was unable to trace, it was sometimes emitted and sometimes not, even under circumstances which, to all appearance, were perfectly similar.

V. In the *urine* of animals which had taken single or repeated doses of the alcohols, the odour of the alcohol itself was in some cases perceptible, in others not; but no distinct indications of formic or valerianic acid were ever found in it.

A few experiments with *valerianic* and *butyric* acid showed that these volatile acids of the series  $C_n H_n O_4$  (a fact long known in the case of acetic and formic acid), when introduced into the stomach in the concentrated state, produce violent inflammation of the mucous membrane, with local softening and hæmorrhage, viz. at the "Fundus."

In conclusion, the author states his intention of instituting similar experiments with acids analogous to benzoic acid, with respect to which an interesting question arises, viz.: whether these acids pass into the urine in the form of hippuric acid (as is stated to be the case with cinnamic acid), or whether after their administration the urine becomes charged with analogous, but not identical, conjugate acids.

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On the Passage of Cumic Acid through the Animal System.

By A. W. Hofmann.

Some observations lately made by J. Schlossberger on the physiological action of organic substances analogously constituted, reminded me of a few experiments commenced several years ago, but interrupted by other researches.

Some investigations of the derivatives of cumic acid (cumol, nitrocumol, cumidine and cumonitrile) carried out in my laboratory, and exhibiting in an unmistakeable manner the perfect parallelism of this series with the compounds derived from benzoic acid, suggested the idea of studying the influence of the animal organism upon that acid. Shortly after Mr. Alex. Ure had made the remarkable observation that benzoic acid, introduced into the organism, is found again in the urine in the form of hippuric acid, the department, under the same circumstances, of cinnamic acid, so closely allied to benzoic acid, was studied by MM. Erdmann and Marchand.

These chemists ascertained that cinnamic acid is likewise converted in its passage through the organism into hippuric acid, an observation which has been lately confirmed by the experiments of Wöhler and Frerichs. This result might have been anticipated if we recollect how readily cinnamic acid is transformed into benzoic acid by the influence of oxidizing agents.

The homology of cuminic acid with benzoic acid appeared to promise a different result. This acid has been converted into benzoic acid only by very indirect processes, namely by the removal of carbon by the action of the alkaline earths, and treatment of the resulting carbohydride with nitric acid. It was not improbable that the passage of this acid through the organism would give rise to the secretion in the urine of an acid homologous to hippuric acid, of a glyco-coll-cuminic acid, and it was with the hope of obtaining this acid that the experiment was made.

After having satisfied myself, by experiments with rabbits, that cuminic acid is perfectly innoxious, I took in the evening several grammes of this acid without feeling the slightest inconvenience. Several others making a similar experiment, I rapidly procured the quantity of urine necessary to operate upon. It was evaporated on the water-bath to the consistence of a syrup, when yellow needles were deposited, which, after re-crystallization with animal charcoal, were found to be pure cuminic acid. In order to fix this result by a number, the purified acid was subjected to combustion.

0.2478 grm. of acid gave :  
 0.6586 " " carbonic acid, and  
 0.1640 " " water.

	Theory.		Experiment.
20 equivs. of Carbon . . .	120	73.19	72.66
12 " " Hydrogen . . .	12	7.33	7.37
4 " " Oxygen . . .	32	19.48	—
1 equiv. " Cuminic acid .	164	100.00	

From the preceding experiment, it is evident that the cuminic acid, unlike benzoic acid, passes through the organism without undergoing any change. The experiment was repeated several times with the same result; the amount also of acid deposited from the urine very nearly agreed with the quantity taken, considering the loss which is unavoidable under such circumstances. I did not succeed in detecting, together with cuminic acid, another peculiar acid in the urine.

The unfavourable result obtained with cuminic acid, induced me to try the same experiment with an acid still nearer allied to benzoic acid. Cuminic acid differs from benzoic acid by 3 ( $C_3 H_3$ ) whilst toluylic acid, discovered by Mr. Noad, contains only  $C_2 H_2$  more than benzoic acid.

Cuminic acid . . . .	$C_{20} H_{12} O_4$
	$C_{18} H_{10} O_4$
Toluylic acid . . . .	$C_{16} H_8 O_4$
Benzoic acid . . . .	$C_{14} H_6 O_4$

Toluylic acid also was found to be perfectly innoxious and could be taken to the amount of several grammes without inconvenience. I was unable to detect any toluylic acid in the urine. On treating, however, the urine with ether, a small quantity of an indifferent substance was dissolved, which crystallized after the evaporation of the latter in perfectly regular and highly lustrous crystals. The great difficulty of obtaining larger quantities of toluylic acid free from nitrotoluylic acid has prevented me from entering into a complete investigation of the crystalline compound.

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**Researches on the Volatile Oils obtained in the Distillation of Wood.**

**By A. Cahours.\***

When crude commercial wood-spirit is mixed with water, a pale-yellow volatile oil separates from it, and rises to the surface of the liquid. This oil is not a pure, definite compound; in fact, when submitted to distillation, it begins to boil at about  $90^{\circ} C.$ , while the last portions do not pass over below  $200^{\circ}$ . The ultimate analysis and vapour-density of these products affording no satisfactory information respecting their constitution, the crude-oil was agitated with concentrated sulphuric acid, whereby it was separated into a brown-red viscid mass, and a clear liquid, having an aromatic odour, the latter floating on the top. The clear liquid, when washed with an alkaline ley, then diluted, dried over fused chloride of calcium, and distilled from anhydrous phosphoric acid, began to boil at  $108^{\circ} C.$ ; the last portions distilled over between  $160^{\circ}$  and  $170^{\circ}$ . A considerable portion of this product passed over between  $108^{\circ}$  and  $112^{\circ}$ ; this was

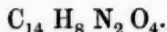
\* Compt. Rend. XXX, 320.

collected apart. Other fixed boiling-points were likewise obtained; one between  $128^{\circ}$  and  $130^{\circ}$ ; another between  $145^{\circ}$  and  $148^{\circ}$ ; the last between  $164^{\circ}$  and  $168^{\circ}$ .

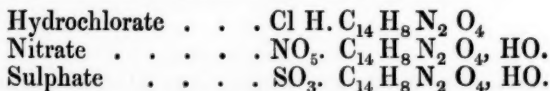
The product, which boils between  $108^{\circ}$  and  $110^{\circ}$ , is *Toluol* (Deville's benzoene),



The mean of several vapour-densities of this compound was found to be equal to 3.27; it represents 4 volumes of vapour, and accords very nearly with the theoretical density, 3.24. To establish completely the identity of this substance with toluol, it was treated with fuming nitric acid: the products thereby obtained were mononitro-toluol and binitro-toluol. The former of these, treated with an alcoholic solution of hydrosulphate of ammonia, yielded toluidine, possessing all the properties ascribed to it by its discoverers; the second is transformed into a new alkaloid, called *Nitro-toluidine*, the formation of which has been previously mentioned by M. Cahours, in a note relating to anisol; its formula is

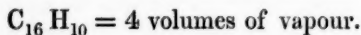


This alkaloid, which crystallizes in yellow needles, yields, with hydrochloric, nitric, sulphuric, and phosphoric acid, definite compounds, the formulæ of which, as determined by analysis, are:



Treated with chloride of benzoyl, or chloride of cumyl, it yields compounds analogous to the amides and anilides.

The product, which boils between  $128^{\circ}$  and  $130^{\circ}$ , exhibits properties closely resembling those of toluol, differing from it in fact only by containing a larger quantity  $C_3H_2$ : it is therefore an homologue of toluol. Several analyses and three vapour-densities, perfectly agreeing among themselves, lead to the formula



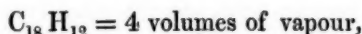
To this compound M. Cahours gives the name of *Xylol* or *Xylene*. Treated with fuming nitric acid, it yields products analogous to those obtained from toluol. *Mononitroxylol*, when dissolved in alcohol, and treated with hydrosulphate of ammonia, yields a base analogous to toluidine; it may be called *Xylidine*.

The liquid which boils at  $148^{\circ}$  exhibits the composition and all the properties of cumol,



The analyses and vapour-densities agree perfectly with this formula. To demonstrate the identity of this substance with cumol, it was treated with fuming nitric acid, and yielded two compounds, presenting all the properties of mononitro-cumol and binitro-cumol; the latter compounds treated with hydrosulphate of ammonia yielded cumidine and nitro-cumidine.

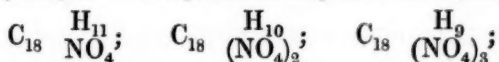
M. Cahours has likewise repeated the investigation of mesitolol, and found that it boils between  $162^{\circ}$  and  $164^{\circ}$  C.; his experiments confirm the composition assigned to this compound by Dr. Hofmann, namely,



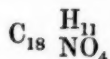
(*Vide* p. 17 of this volume). Mesitolol is isomeric, but not identical with cumol; for not only does its boiling-point differ considerably from that of cumol, but it likewise gives totally different products by contact with various reagents. Under the influence of fuming nitric acid, it yields three distinct products, viz.:—

1. *Mononitro-mesitolol*, when the acid is not used in excess, and especial care is taken to keep the reacting substances cool. 2. When more nitric acid is used, and the temperature is allowed to rise, the product is *Binitro-mesitolol*, a compound discovered by Dr. Hofmann. 3. When, instead of nitric acid, a mixture of nitric acid and fuming sulphuric acid, is used, the product is *Trinitro-mesitolol*, a substance whose formation and properties are described by M. Cahours in a memoir on the action of a mixture of sulphuric and nitric acid on organic substances.\*

Hence it appears that mesitolol, by contact with nitric acid, gives rise to three products, derived by substitution of hyponitric acid vapour for hydrogen: these products may be thus expressed:



The first of these bodies, viz., mononitro-mesitolol, when treated with an alcoholic solution of potash, becomes heated, and evolves two products on distillation. One of these is a liquid, which is formed in very small quantities only, and possesses the properties of an alkaloid; the other, which is solid, dissolves very readily in alcohol, and separates from it by spontaneous evaporation in tubular crystals of great beauty. Its composition, as found by analysis, corresponds to the formula

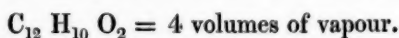


It is, therefore, isomeric with mononitro-mesitolol.

\* Ann. Ch. Pharm. LXIX, 230.

The last hydrocarbon obtained by treating the volatile oil of wood with sulphuric acid, that namely, which boils between  $164^{\circ}$  and  $168^{\circ}$ , has exactly the composition of cumol and mesitolol; its condensation is, moreover, the same as that of these bodies, and yet it is not identical with either.

It appears, then, that the volatile oil which is produced in the distillation of wood, and contaminates the ordinary wood-spirit of commerce, contains hydrocarbons identical with those which are obtained in the distillation of coal-tar, and which have been lately examined by Mr. Mansfield. These results, establish an intimate relation between coal, and the woody matter which may be regarded as its origin.—In certain specimens of wood-spirit, the author has found an oil much more volatile than the preceding; it begins to boil at about  $58^{\circ}$  C. the last portions distilling over between  $90^{\circ}$  and  $100^{\circ}$ . This very volatile oil is almost wholly composed of two substances: the one, which constitutes about three-fourths of it, is the acetate of methyl, as shown by its ultimate analysis, the density of its vapour, and its behaviour with reagents; the other possesses the properties and composition of Fremy's metacetone:




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On the Formation of Succinic Acid by the Oxidation of Butyric Acid.

By M. Dessaignes.\*

Gerhardt, in his "Précis de Chimie Organique," has remarked that, parallel to the series of monobasic fatty acids, whose general formula is  $C_n H_n O_2$ , there may also be formed a series of bibasic acids, according to the formula  $C_n H_{n-2} O_4$ . Almost all the acids of these two parallel series are produced simultaneously when fatty bodies of high combining number are oxidized by nitric acid; and it may be conceived that each term of the bibasic series is formed by simple oxidation of the corresponding term in the monobasic series; but, excepting in the case of acetic and oxalic acid, the possibility of this transformation had yet to be demonstrated by experiment.

Succinic acid in the one series is collateral to butyric acid in the other; and Dessaignes has, in fact, succeeded in forming the first of these acids by the oxidation of the second. In an apparatus,

\* Compt. Rend. XXX, 49.



consisting of a retort and a long tube, serving both for adapter and receiver—the junctions being ground with emery, and the connection made without the use of cork—30 grammes of very pure butyric acid prepared by the fermentation of flesh and fecula, was heated with twice its volume of nitric acid of specific gravity 1.40. The apparatus was inclined in such a manner, that the condensed vapours of the butyric acid constantly fell down again into the retort, and nitric acid was added from time to time. Although the mixture was continually surmounted by a red atmosphere of nitrous gas, the action was very slow, and was far from being complete, even after continuing for ten days of twenty-four hours each. Finally, when the red vapours were no longer visible, the liquid was cautiously distilled, till a crystalline residue was obtained. This residue was soiled with a substance which attracted moisture from the air, and from which it could not be purified by prolonged heating in the water-bath; it was alternately purified by pressure between folds of paper. The crystals, when thus purified, presented all the physical characters and chemical reactions of succinic acid. The quantity obtained was not sufficient to allow of its complete purification for the purpose of ultimate analysis; but a silver-salt was prepared, and gave by calcination 64.33 per cent of silver, the calculated quantity being 65.05.

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On the Formation of Aspartic Acid from Bimalate of Ammonia.

By M. Dessaignes.\*

We are indebted to Piria for the interesting observation, that asparagin and aspartic acid, when submitted to the oxidizing action of nitrous gas, disengage nitrogen, and leave a residue of malic acid. From this, it follows that these two bodies may be regarded as amides of malic acid, corresponding, for example, to oxamide and oxamic acid. If this be the case, we ought to be able to reproduce asparagin and aspartic acid synthetically. The action of ammonia on malic ether ought to produce asparagin. The author did not succeed in his attempts to prepare malic ether, but he has obtained aspartic acid by means of the bimalate of ammonia.

When bimalate of ammonia is heated in the oil-bath to 160° —

\* Compt. Rend. XXX, 324.

200° C., it fuses with intumescence, and disengages water very slightly impregnated with ammonia. The residue is a reddish, transparent, and somewhat resinous mass, which is but very slightly soluble in water, even at a boiling heat. By repeated washings with warm water, an amorphous, pulverulent substance is obtained, having a pale brick-red colour, and an earthy taste. This substance is a new azotized acid, which differs in all its reactions from aspartic acid; it is very stable. It dissolves in concentrated acids on the application of heat, and is precipitated unchanged from the solution by water, even after boiling for a few moments. But when heated for five or six hours with nitric or hydrochloric acid, it undergoes a remarkable transformation. The action is complete when no further precipitate is formed on the addition of water. The solution, when evaporated to dryness in the water-bath, leaves a brown, crystalline, strongly acid residue, which is a compound of hydrochloric acid and an organic substance. This compound is easily purified by means of charcoal, and is then obtained in beautiful, colourless crystals. On dissolving these crystals in a tolerably large quantity of warm water, dividing the solution into two equal parts, neutralizing one of them exactly with ammonia, and adding it to the other, the liquid yielded, on cooling, a quantity of small brilliant prisms, consisting of aspartic acid. The acid thus obtained does not agree in crystalline form with aspartic acid obtained from asparagin; but the salts which it forms with lime, soda, and the oxides of copper and silver, crystallize in the same forms as the corresponding aspartates, and yield, by analysis, the same quantity of base. The crystallized acid itself likewise yields by ultimate analysis the same numbers as those obtained by the combustion of aspartic acid.

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**On the Fibrin of Muscular Flesh.**

**By Justus Liebig.\***

When very finely chopped meat is freed by digestion in cold water and pressure from all its soluble ingredients, there remains a white tasteless residue, consisting of true muscular fibre, together with nervous and cellular tissue. Muscular fibre is generally considered to be identical with the fibrin of blood; this, however, is an error, arising, perhaps, from the close resemblance between the physical properties of the two substances.

\* Ann. Ch. Pharm. LXXIII, 125.

When blood-fibrin is immersed in water, containing  $\frac{1}{10}$  per cent of hydrochloric acid, it quickly swells up to a gelatinous mass; if stronger acid be added, the jelly shrinks up again nearly to its former bulk, but if subsequently immersed in pure water, swells up like a sponge. This experiment may be repeated several times, without occasioning the solution of any perceptible quantity of blood-fibrin in the liquid.

The fibrin of muscular flesh behaves in a totally different manner. When it is immersed in water containing the above-mentioned proportion of acid, the greater part dissolves immediately and completely, forming a solution rendered slightly turbid by fatty particles, which, however, may be completely, though with difficulty, separated by filtration; the filtered liquid is perfectly clear. The solution of the fibrin takes place at ordinary temperatures. The liquid, when neutralized, coagulates to a thick, white, gelatinous mass, easily soluble in excess of alkali. Common salt and other saline solutions, added to the alkaline solution, produce a coagulum which dissolves on the addition of a large quantity of warm water.

The precipitate obtained on neutralizing the hydrochloric acid solution of the flesh-fibrin is soluble in lime-water, and the solution, when boiled, yields a coagulum like a dilute solution of white of egg. If the precipitate be previously boiled in water, it is rendered insoluble in lime-water. It is especially remarkable that this constituent of muscular flesh, which is so easily soluble in water acidulated with hydrochloric acid, is contained in very unequal quantities in the flesh of different animals. Thus the flesh of poultry, or of oxen, dissolves almost wholly; whereas mutton leaves a considerable residue; and in veal, the insoluble portion considerably exceeds the half. The insoluble residue is elastic and white, but softer and more gelatinous than the original flesh, like blood-fibrin swollen up in slightly acidulated water.

The composition of flesh-fibrin differs from that of blood-fibrin, approaching more nearly to that of albumen. Dr. Strecker found in it: carbon 54.6 and 53.67; hydrogen 7.28 and 7.27; nitrogen 15.84 and 16.26; sulphur 1.21, 1.02 and 1.11; ash 1.4.

Blood-fibrin constitutes only a fraction per cent of blood. According to the most careful analyses, it contains more nitrogen than muscle-fibrin; hence the supposition that it serves for the formation of the latter is very doubtful. An important constituent of blood-fibrin is iron, which is invariably found in it. Liebig has never succeeded in obtaining blood-fibrin free from iron. The absence of iron in this substance has often been asserted, on the ground of its leaving a white ash; but even this colourless ash contains a considerable quantity of iron.

When well washed blood-fibrin is completely immersed in water

contained in a vessel which can be closed, and placed in a warm situation, putrefaction rapidly sets in. The fibrin gradually becomes coloured, loses its coherence, and in about three weeks dissolves completely, forming a very slightly coloured liquid, in which a few black flakes are seen to float about, their colour arising from sulphide of iron; these flakes may be easily separated by filtration. The solution thus obtained is undistinguishable from a solution of albumen; when heated, it coagulates in a gelatinous mass, possessing all the characters of albumen, and likewise the same composition, as appears from an analysis made by Dr. Strecker, which gave: carbon 53.9; hydrogen 6.99; nitrogen 15.58; sulphur 1.59 — 1.45; ash 0.28.

This albumen is probably one of the most remarkable products of putrefaction. During the process of conversion, a very fetid volatile product is formed, together with a small quantity of free hydrogen. The liquid filtered from the coagulated albumen contained a small quantity of an azotized body, not yet further examined.

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**Method of obtaining Metacetic Acid in large quantities.**

**By Fr. Keller.\***

A convenient quantity (2 or 3 lbs.) of bran is mixed to a semi-fluid consistence, with ten times its weight of water at 50°—60° C. (122°—140° F.), and with a fourth-part of coarsely-divided leather (scrapings of tanned ox-hide are the best adapted to the purpose); pounded chalk is then added, and the whole left to ferment in a warm place. The process is complete in the course of three or four weeks in winter, and in a few days in summer; its termination is indicated by the sinking together of the mass, which was previously spongy and intumescent. The mass is then strained, and washed with hot water; the lime-salt converted into soda-salt; and the acid separated by sulphuric acid. To separate any acetic or butyric acid that might be present, a portion of the liquid was saturated with carbonate of soda, the rest added to it, and the free acid separated from the saline residue by distillation. This residue was found to consist of a mixture of acetate and metacetate of soda. In all subsequent experiments which the author made with the view of discovering the presence of any other acid besides metacetic, the silver-salt prepared from the residue was found to have the same composition, viz.:

\* Ann. Ch. Pharm. LXXIII, 205.

	Calculated.		Found.
C <sub>6</sub> . . . .	36	19.89	19.73
H <sub>5</sub> . . . .	5	2.76	2.72
Ag . . . .	108	59.55	59.32
O <sub>4</sub> . . . .	32	17.80	18.23
	<hr/>	<hr/>	<hr/>
	181	100.00	100.00

The silver-salt when newly prepared may be recrystallized from hot water, without perceptible blackening; but after drying over sulphuric acid, it is for the most part decomposed by boiling with water. The lead-salt prepared by saturating the pure acid with hydrated oxide of lead formed a radiated crystalline mass, which, when heated by the hand, deliquesced to a viscid liquid. The baryta-salt dried up to a gummy mass, but after a while swelled up in cauliflower-like tufts, which effloresced and fell to pieces on exposure to the air. This salt contains 36.38 per cent (9 at.) of water of crystallization, which it loses when heated to 140° C. 1.43 grm. treated with sulphuric acid yielded 1.186 Ba O.  $\text{SO}_3 = 54.42$  per cent baryta. The soda-salt was only once obtained in the crystalline state, after being heated to fusion and then dissolved in the smallest possible quantity of water. It was generally obtained in the form of a greasy mass. All these salts, when thrown upon water in small fragments, exhibit a rotatory movement, similar to that of the butyrates.

#### On the Action of certain Reagents upon Quinine.

By Dr. Vogel, Jun.\*

Brandes has shown that when a solution of sulphate of quinine is mixed with chlorine-water, and caustic ammonia added, the liquid acquires an emerald-green colour. Starting from this experiment, the author has succeeded, by the use of a few other reagents, in producing very characteristic changes of colour in the solution of sulphate of quinine.

If to a solution of sulphate of quinine mixed with chlorine water there be added, instead of ammonia, an excess of concentrated solution of ferrocyanide of potassium, a dark-red colour is immediately produced, and remains unaltered for some hours, but afterwards, especially on exposure to light, passes into green. This reaction of quinine is

\* Ann. Ch. Pharm. LXXIII, 221.

highly characteristic and well-adapted for a lecture experiment. If caustic-potash be used in place of ammonia, the solution acquires a sulphur-yellow colour. Instead of chlorine, a solution of chloride of lime mixed with hydrochloric acid may be advantageously used, in which case, on addition of ammonia, a green powder is precipitated. The preceding reactions are not produced with cinchonine, and may therefore be regarded as marks of distinction between the two alkaloids.

According to the most recent reports of chemists, there appears to be a prospect of preparing the vegetable alkaloids directly from their elements; hence it is much to be desired that characteristic reactions should be discovered—especially such as depend on change of colour—which may serve as standard tests by which the nature of the artificial products may be determined.



THE  
QUARTERLY JOURNAL  
OF THE  
CHEMICAL SOCIETY.

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June 3, 1850.

THOMAS GRAHAM, Esq., V.P., in the Chair.

Dr. D. S. Price, was elected a Fellow of the Society.

The following presents were announced :

"The Pharmaceutical Journal for June:" from the Editor.

"Journal of the Franklin Institute for March and April:" from the Institute.

"Watson's Chemical Essays:" from Mr. Medlock.

The following papers were read :

XX.—*Analysis of the Ashes of the Spanish Potato (Convolvulus Batatas), and of the Eddoes (Arum esculentum Linn. Colocasia esculenta, Schott.)*

By THORNTON J. HERAPATH, F.C.S.

The Spanish or sweet potato and eddoes, although of little or no importance to the English agriculturist, are commonly cultivated for their roots in most, if not in all tropical climates, both in the eastern and western hemispheres. The tubers of these plants, in fact, are employed in large quantities in all the West Indian Islands as food for man and animals, and are looked upon in those countries, as is the potato in our own, being at the same time nutritious, and pleasant to the taste. Only the roots of the former, the batata, however, I am informed, can be made use of by Europeans, those of the latter, particularly when fresh, being extremely acrid, although not so much so as to render them unpalatable to the negroes, with whom they are a common article of food. This acrimony would appear to be caused by the presence of some volatile body, as the

vegetable is said to become sweet and well-tasted after boiling, or when roasted in hot ashes.

Proximate analyses of these plants have been already performed by other chemists,\* but no attempt, as far as I am aware, has ever been made to determine the nature of their inorganic constituents. It was, therefore, with the wish of supplying this desideratum that I undertook the present examination, as I thought my results might possibly be of service to some of those of my fellow-countrymen, who are connected with the interests of our West Indian colonies. For the specimens which I have operated upon, I am indebted to the kindness of my friends, Charles Thornton Coathupe, Esq. of Wraxall, and W. H. Richards, Esq. of Barbadoes, to both of whom I must acknowledge my obligations.

The *modus operandi* employed in the preparation and analysis of these ashes has been already fully explained in some of my former papers, which have been communicated to the Society.

#### I.—SPANISH POTATO OR BATATA.

749·54 grs. of the fresh roots, cut into thin slices, gave 249·34 grs. of dried vegetable matter, and furnished upon incineration 11·996 grs. of ash. Subsequent analysis, however, proved that this ash contained 0·690 grs. of charcoal and sand; consequently, the true inorganic constituents amounted to 11·306 grs. in weight = 1·50849 per cent, numbers which correspond to:

Water and other volatile matters	. 66·7340
Vegetable matter . . .	. 31·7575
Inorganic constituents . . .	. 1·5085
	<hr/>
	100·000

The proportion per cent of ash from the dried plant, therefore, amounted to 4·5347.

The 11·996 grs. of ash obtained as above, were found, upon analysis, to be composed of:

Substances soluble in water (A)	. . 7·883
„ insoluble „ (B)	. . 4·113

The solution A, when treated with re-agents, gave:

Carbonic acid . . . . .	0·9800
Sulphate of baryta . . . . .	2·3700 = SO <sub>3</sub> 0·8030

\* O. Henry, J. Pharm. [3] XI, 233.

Phosphate of baryta (3 BaO.

$\text{PO}_5$  . . . . . 0.4500 =  $\text{PO}_5$  0.1058

Chloride of silver . . . . . 5.7600 = Cl 1.4400

Mixed chlorides of potassium  
and sodium . . . . . 8.0770

Potassio-chloride of platinum. 22.066 = KCl 6.7897 = KO 4.2786

Chloride of sodium (by loss) . . . . . 1.2873 = NaO 0.6868

Quantities which are equivalent to :

Carbonate of potash . . . . . 3.118 = 27.5763 p. c. of ash.

Sulphate of potash . . . . . 1.766 = 15.6243 " "

Phosphate of potash (3 KO.

$\text{PO}_5$ ) . . . . . 0.302 = 2.6771 " "

Chloride of potassium . . . . . 1.407 = 12.4465 " "

Chloride of sodium . . . . . 1.287 = 11.3904 " "

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7.880 = 69.7146

The substances insoluble in water (B) furnished :

Carbonic acid . . . . . 0.7040

Sulphate of baryta . . . . . traces  $\text{SO}_3$  . traces

Earthy phosphates, &c. . . . . 1.626

Perphosphate of iron . . . . . 0.346 =  $\begin{cases} \text{PO}_5 & . & 0.1988 \\ \text{Fe}_2 \text{O}_3 & . & 0.1472 \end{cases}$

Phosphate of alumina . . . . . traces

Pyrophosphate of magnesia. 1.335 =  $\text{PO}_5$  . 0.8009

Carbonate of lime . . . . . 2.449 = CaO . 1.3719

Pyrophosphate of magnesia. 0.404 =  $\text{MgO}$  . 0.1613

Silica . . . . . 0.2400

Charcoal, sand, &c. . . . . 0.6870

They were consequently composed of :

Carbonate of lime . . . . . 1.334 = 11.7970 p. c. of ash.

Carbonate of magnesia. 0.224 = 1.9828 " "

Sulphate of lime . . . . . traces = traces " "

Perphosphate of iron . . . . . 0.346 = 3.0595 " "

Phosphate of alumina . . . . . traces = traces " "

Phosphate of lime

(3 CaO.  $\text{PO}_5$ ) . . . . . 1.160 = 10.2590 " "

Phosphate of magnesia. 0.120 = 1.0613 " "

Silica . . . . . 0.240 = 2.1258 " "

Charcoal, sand, and loss. 0.689 = deducted

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4.113 = 30.2854

The percentage-composition of the ash of this plant, after deduction of the charcoal, sand, and carbonic acid, may be expressed as follows :

SOLUBLE SALTS :

CO <sub>2</sub>	.	.	.	8.6671	After deducting the CO <sub>2</sub> .
SO <sub>3</sub>	.	.	.	7.1018	8.3448
PO <sub>5</sub>	.	.	.	0.9357	1.0324
KO	.	.	.	29.3490	34.4848
NaO	.	.	.	—	—
KCl	.	.	.	12.4465	14.5070
NaCl	.	.	.	11.3904	13.3848

INSOLUBLE SALTS :

CO <sub>2</sub>	.	.	.	6.2289	—
SO <sub>3</sub>	.	.	.	traces	traces
PO <sub>5</sub>	.	.	.	7.0720	8.3769
CaO	.	.	.	11.9545	14.2543
MgO	.	.	.	1.4265	1.6761
Fe <sub>2</sub> O <sub>3</sub>	.	.	.	1.3018	1.5297
Al <sub>2</sub> O <sub>3</sub>	.	.	.	traces	traces
SiO <sub>3</sub>	.	.	.	2.1258	2.4092
				100.0000	100.0000

II.—EDDOES OR EDDOW.

749.18 grs. of the fresh root, when dried and incinerated, furnished 12.729 grs. of ash, which was afterwards found to contain 0.39 grs. of carbon and sand; consequently, the true weight of ash was equal to 12.339 grs. = 1.6470 per cent.

These 12.729 grs. of ash, when treated with hot water, were resolved into :

Substances soluble in water (A)	.	.	.	.	7.854
„ insoluble „ (B)	.	.	.	.	4.875

The aqueous solution (A), when treated in the usual manner, afforded of :

Carbonic acid	.	.	.	.	.	.	.	1.2820
Sulphate of baryta.	.	.	.	1.187 = SO <sub>3</sub>	.	.	.	0.4025
Phosphate of baryta								
(3 BaO. PO <sub>5</sub> )	.	.	.	2.147 = PO <sub>5</sub>	.	.	.	0.5090
Chloride of silver	.	.	.	2.070 = Cl	.	.	.	0.5175
Mixed chlorides of potassium and sodium	.	.	.	8.460				

Potassio-chloride of platinum  $23.376 = \text{KCl} = 7.597 = \text{KO } 4.7981$

Chloride of sodium (by loss) . . . . .  $0.863 = \text{NaO } 0.4603$

Quantities of which are equivalent to :

Carbonate of potash . . . . .  $4.0791 = 33.0532$  p. c. of ash.

Sulphate of potash . . . . .  $0.8855 = 7.1752$  " "

Phosphate of potash (tribasic)  $2.0270 = 16.4249$  " "

Chloride of sodium . . . . .  $0.8630 = 6.9929$  " "

The substances insoluble in water (B) gave, upon analysis :

Carbonic acid . . . . .  $0.4430$

Sulphate of baryta .  $0.399 = \text{SO}_3$  . . .  $0.1353$

Earthy phosphates, &c.  $2.616$

Perphosphate of iron .  $0.230$  .  $\left\{ \begin{array}{l} \text{PO}_5 \text{ . . . } 0.1089 \\ \text{Fe}_2 \text{ O}_3 \text{ . . } 0.1211 \end{array} \right.$

Phosphate of alumina . traces

Pyrophosphate of magnesia  $1.837 = \text{PO}_5$  . . .  $1.1023$

Carbonate of lime . .  $3.467 = \text{CaO}$  . . .  $1.9421$

Pyrophosphate of magnesia, traces =  $\text{MgO}$  . . traces

Silica . . . . .  $0.633$

Charcoal and sand . .  $0.390$

They were therefore composed of :

Carbonate of lime . . . . .  $1.0070 = 8.1590$  p. c. of ash.

Carbonate of magnesia . . traces = traces " "

Sulphate of lime . . . . .  $0.2300 = 1.8637$  " "

Perphosphate of iron . . .  $0.2300 = 1.8637$  " "

Phosphate of alumina . . . traces = traces.

Phosphate of lime (tribasic) .  $2.3860 = 18.2223$  " "

Phosphate of magnesia . . traces = traces.

Silica . . . . .  $0.6320 = 5.2451$  " "

Charcoal and sand . . . . .  $0.3900 =$  deducted

$\underline{4.8750} \quad \underline{35.3538}$

After deducting the carbon and sand and carbonic acid, the composition of the ash of the eddoes may therefore be stated as follows :

#### SOLUBLE SALTS :

$\text{CO}_2$  . . . . .  $10.3921$  . . . . . After deducting  $\text{CO}_2$

$\text{SO}_3$  . . . . .  $3.2614$  . . . . .  $3.7879$

$\text{PO}_5$  . . . . .  $4.0920$  . . . . .  $4.7526$

$\text{KO}$  . . . . .  $38.8790$  . . . . .  $45.1440$

$\text{NaO}$  . . . . . — . . . . . —

$\text{KCl}$  . . . . . — . . . . . —

$\text{Na Cl}$  . . . . .  $6.9929$  . . . . .  $8.1218$

$\underline{63.6174}$

$\underline{53.8063}$

Soluble Salts . . . . 63·6174 . . . . 53·8063

INSOLUBLE SALTS:

CO <sub>2</sub> . . . . .	3·5086 . . . . .	—
SO <sub>3</sub> . . . . .	1·0963 . . . . .	1·2732
PO <sub>5</sub> . . . . .	9·8144 . . . . .	11·3990
CaO . . . . .	15·7369 . . . . .	18·2774
Mg O . . . . .	traces . . . . .	traces
Fe <sub>2</sub> O <sub>3</sub> . . . . .	0·9813 . . . . .	1·1397
Al <sub>2</sub> O <sub>3</sub> . . . . .	traces . . . . .	traces
SiO <sub>3</sub> . . . . .	5·2451 . . . . .	6·1044

100·0000

100·0000

Now, if we compare the results of the two analyses just recorded with those of my former examination of potato-ashes,\* we shall observe a very close resemblance between them; in fact, the ashes of all these three plants evidently belong to the same class, namely, to that in which the alkaline carbonates predominate. Reasoning from this circumstance alone then, we should be led to expect that the same species of soil would be suitable for the cultivation both of the potato, eddoes and batata; and such, I am informed, is the fact.

The ashes of the potato, however, we shall find, contain a much larger proportion of alkalis and phosphoric acid than either of the others; and we should hence at first be induced to believe that the former plant would prove a more exhausting crop than the eddoes or batata; but a little calculation will show us that this would be an erroneous conclusion; in fact, just the opposite is the case, as will be readily seen upon consulting the following table:

TABLE I. Showing the amounts of the several inorganic constituents removed from the soil in a ton weight of each crop:

	Batata.		Eddoes.		Potato.†	
Sulphuric acid . . . .	2 lbs.	6¼ oz.	1 lb.	13 oz.	1 lb.	2½ oz.
Phosphoric acid . . . .	2	11¼	5	1	3	7½
Potash . . . . .	9	14½	14	2½	13	9
Chloride of potassium . .	4	2¾	—	—	—	—
Chloride of sodium . . .	3	13½	2	2	0	1¼
Lime . . . . .	4	1½	5	15	0	11½
Magnesia . . . . .	0	7¾	a little		0	15
Oxide of iron . . . . .	0	7	0	5¾	} small quantities.	
Silica . . . . .	0	11½	1	14½		
	28 lbs. 15 oz.		31 lbs. 5¾ oz.		19 lbs. 14¾ oz.	

\* Chem. Soc. Qu. J. II, 21.

† This calculation was made by taking the mean of the five analyses given in the paper just referred to.



TABLE II. Giving formulæ from artificial manures required by the same quantity of each vegetable :\*

	Batata.		Eddoes.		Potato.	
Pearl-ash	18 lbs.	4 oz.	19 lbs.	12½ oz.	19 lbs.	12 oz.
Epsom-salts ( $\text{MgO} \cdot \text{SO}^3 + 7\text{HO}$ )	3	5½	—	—	7	10
Glauber-salts ( $\text{NaO} \cdot \text{SO}^3 + 10\text{HO}$ )	4	0	5	1	—	—
Common salt	7	2½	2	2	0	1½
Gypsum ( $\text{CaO} \cdot \text{SO}^3 + 2\text{HO}$ )	4	5½	0	13	—	—
Bone earth	5	13½	10	10	7	8½

Burnt bones	6 lbs.	5 oz.	11 lbs.	15 oz.	8 lbs.	7½ oz.
Bones (half-inch)	9	13½	18	6	12	9½

The relative powers of exhaustion (if 1 may be allowed to use the expression) of these three crops for the most important of the inorganic constituents—the alkalis and phosphoric acid—may therefore be represented by the following numbers :

	Alkalis.†		Phosphoric acid.	
Potato	217	or 1000	55½	or 1000
Eddoes	244½	or about 1126¾	81	or about 1459
Batata	233	„ 1073¾	43¼	„ 779

## XXI.—On the Bichromate of Ammonia, and some of its Double Salts.

BY MESSRS. HENRY R. RICHMOND AND JOHN S. ABEL,  
*Of the Royal College of Chemistry.*

Being engaged, a few weeks since, in preparing some of the double salts of chromic acid, described by Mr. S. Darby, in the Quarterly Journal of the Chemical Society,‡ we were struck by the unusual and somewhat improbable nature of the formula,  $\text{NH}_3 \cdot 2\text{CrO}_3$ , assigned by him to the bichromate of ammonia. We, therefore, prepared a specimen of the salt, and made several analyses of it, the details of which are given below. We also prepared and analysed several double compounds which the bichromate of ammonia forms with protochloride of mercury.

### BICHROMATE OF AMMONIA.

The bichromate of ammonia was prepared according to the directions given by Mr. Darby. A strong solution of chromic acid was

\* In the construction of these formulæ, the oxide of iron and silica were not taken into consideration, as it was supposed that all soils contain these substances in sufficient quantity to supply the wants of any plant not belonging to the *gramineæ*.

† Including the alkaline chlorides, and regarding them as free alkalis.

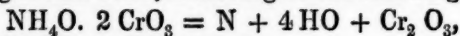
‡ Vol. I. p. 20.

divided into two equal portions, one of which was saturated with ammonia; the two solutions were then mixed and evaporated.

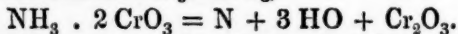
As the chromic acid employed contained a large quantity of sulphuric acid, the product of the first crystallization was very impure. It was of a brown colour, but became perfectly yellow and opaque on drying. This curious change could also be produced at once by pouring water over the crystals.

After several recrystallizations, the colour changed to a beautiful red, and the crystals no longer became opaque under any circumstances. For analysis, they were powdered and dried *in vacuo* over sulphuric acid.

In determining the quantity of chromic acid, we availed ourselves of the remarkable deportment of this salt when exposed to the influence of heat. Under these circumstances, the salt is decomposed with evolution of nitrogen and water, according to the following equation:



or, if we take the formula  $\text{NH}_3 \cdot 2 \text{CrO}_3$ ,



This decomposition was observed at an early period by Hayes, and lately again by Böttger, who noticed that the sesquioxide, separated in this reaction, presents a very peculiar appearance, closely resembling mixed tea.

In order to avoid all loss from the violent evolution of steam and nitrogen, which was apt to scatter portions of the sesquioxide, it was found convenient to insert a plug of asbestos into the glass tube in which the operation was performed: the tube was subsequently drawn out, so as to leave only a small opening for the escape of the gases.

The ammonia determinations were made in the following manner: a weighed portion of the substance was dissolved in a small quantity of water in a porcelain dish; hydrochloric acid and alcohol were added to reduce the chromic acid; and the ammonia was precipitated by means of bichloride of platinum. After evaporating nearly to dryness, the residue was thrown on a filter, and the sesquichloride of chromium was removed by washing in the usual way with a mixture of alcohol and ether, in which it is readily soluble.

Several other methods of determining the ammonia were tried without success. One of these consisted in distilling the bichromate with a solution of potassa, the liberated ammonia being collected in the ordinary nitrogen bulbs. The results of this process were always too low, owing to a portion of the ammonia remaining in the solution.

In addition to the determinations of chromic acid and ammonia, several hydrogen determinations were made by burning the salt with chromate of lead.

We have given below the calculated percentages of chromic acid and of ammonia for the formulæ  $\text{NH}_3 \cdot 2 \text{CrO}_3$ , and  $\text{NH}_4\text{O} \cdot 2 \text{CrO}_3$ . It will be seen that the results of all the analyses agree pretty closely with the latter formula.

Theoretical percentages :

	Formula $\text{NH}_3 \cdot 2 \text{CrO}_3$ .		Formula $\text{NH}_4\text{O} \cdot 2 \text{CrO}_3$ .	
Chromic acid . . .	104.30	85.98	104.30	80.05
Ammonia . . . .	17.00	14.02	17.00	13.05
Water . . . . .	—	—	9.00	6.90
	<hr/>	<hr/>	<hr/>	<hr/>
	121.30	100.00	130.30	100.00

Details of analyses:

#### CHROMIC ACID DETERMINATIONS.

- I. 0.8753 grm. of salt gave 0.5393 grm. of sesquioxide of chromium  
 II. 0.624 " " " 0.385 " " "  
 III. 0.2273 " " " 0.1409 " " "

#### AMMONIA DETERMINATIONS.

- IV. 0.3682 grm. of salt gave 0.641 grm. of the platinum-salt  
 V. 0.1198 " " " 0.2043 " " "  
 VI. 0.2185 " " " 0.3767 " " "  
 VII. 0.2515 " " " 9.4332 " " "

The percentage of chromic acid and ammonia calculated from these analyses is tabulated below.

Calculated percentages :

	I.	II.	III.	IV.	V.	VI.	VII.*
Chromic acid	80.03	80.14	80.40	—	—	—	—
Ammonia	—	—	—	13.11	12.99	13.09	13.08

#### HYDROGEN DETERMINATIONS.

- VIII. 2.8217 grm. of the salt gave 0.8165 grm. of water

- IX. 2.0455 " " 0.5752 " "

The theoretical percentage of hydrogen for the formula  $\text{NH}_3 \cdot 2 \text{CrO}_3$  is 2.47.

The theoretical percentage of hydrogen for the formula  $\text{NH}_4\text{O} \cdot 2 \text{CrO}_3$  is 3.07.

Analyses VIII. and IX. give respectively 3.21 and 3.12 per cent, agreeing with the latter formula.

In all the calculations, we have taken the equivalent of chromium as 28.15, instead of 26.3, which is the number adopted by Mr. Darby. The latter supposition reduces the theoretical percentage of chromic acid, according to either formula, by about 0.5, and slightly increases the percentage of chromic acid deduced from the amounts of sesquioxide of chromium found in the analyses. These discrepan-

cies, however, are by no means sufficient to account for the great difference between our results and those of Mr. Darby. We have made a few experiments, in order to ascertain whether the compound in question might lose an equivalent of water at  $100^{\circ}$ , and thus give rise to the formation of the substance which has been analysed by Mr. Darby: we have not, however, succeeded in obtaining such a compound. Leaving it, therefore, doubtful whether such a body actually exists, we do not hesitate to conclude, from the results of our own analyses, that a compound of the formula  $\text{NH}_4 \text{O} \cdot 2\text{CrO}_3$  does exist, exactly corresponding to the potassa-salt,  $\text{KO} \cdot 2\text{CrO}_3$ , with which it is most likely isomorphous.

DOUBLE COMPOUNDS OF BICHROMATE OF AMMONIA WITH PROTO-  
CHLORIDE OF MERCURY.

Having satisfied ourselves with respect to the constitution of the bichromate of ammonia, we next turned our attention to the double salt which it forms with protochloride of mercury, and to which Mr. Darby has assigned the formula  $\text{NH}_3 \cdot 2 \text{CrO}_3 \cdot \text{HgCl}$ .

This salt presents itself in very different forms, according to the strength of the solution from which it is crystallized. The first specimen which was prepared was deposited from a concentrated solution in the form of small red needles, closely resembling those of the bichromate of chloride of potassium. Several analyses of this salt gave rather uncertain results, approaching, however, most nearly to Mr. Darby's formula. As it seemed probable that a small quantity of uncombined protochloride of mercury was mixed with the salt, we prepared another specimen in the following manner. About equal weights of the two salts were dissolved together in rather a large quantity of water; the solution being allowed to cool, a portion of the protochloride of mercury separated and was removed. The solution was then evaporated down just sufficiently to cause the formation of a few crystals on cooling. The salt obtained in this manner crystallized in beautiful, large, six-sided prisms of a splendid red colour. The crystals were dried on blotting-paper, and afterwards *in vacuo* over sulphuric acid.

On further evaporation, the liquid yielded a second crop of crystals, in appearance exactly the same as the first, which were likewise removed and dried. The mother-liquor was once more evaporated, and on cooling deposited some more beautiful red crystals, very much resembling the other crops, but rather more inclined to the needle-shape; these crystals were also preserved and dried. On attempting to recrystallize portions of these salts, it was found that a part of the protochloride of mercury crystallized out by itself,—

whence it appears that it is necessary to have an excess of bichromate of ammonia in the solution, to obtain the salts free from uncombined protochloride of mercury.

The products of these three crystallizations were analysed successively in the order in which they were deposited. They all deflagrated on heating, the protochloride of mercury being driven off, together with the water of the nitrogen resulting from the decomposition of the bichromate of ammonia, and pure sesquioxide of chromium remaining behind: the first two salts deflagrated gently, leaving the sesquioxide of chromium in the form of a dark powder, which became green when strongly heated; the third salt deflagrated violently, swelling up to a great bulk, and leaving the sesquioxide in large flakes of a dull green colour, assuming the most fantastic shapes.

#### CHROMIC ACID DETERMINATIONS BY IGNITION.

The chromic acid in these salts was determined in nearly the same manner as in the bichromate of ammonia; but as they did not deflagrate with such violence as the latter salt, and as it was necessary to apply a strong heat to drive off the whole of the protochloride of mercury, the operation was performed in a porcelain crucible instead of a glass tube.

#### DETERMINATIONS OF MERCURY AND CHROMIC ACID.

The mercury was determined as protosulphide, the chromic acid being reduced by means of hydrochloric acid and alcohol before passing the hydrosulphuric acid, in order to avoid the precipitation of free sulphur. The chromic acid was also determined, in the usual way by precipitating the sesquioxide by means of ammonia, in the filtrate from the protosulphide of mercury.

#### HYDROGEN DETERMINATIONS.

In making the hydrogen determinations, some precautions were necessary, for if the chloride of calcium tube had been placed as usual, close to the combustion furnace, the mercury would have been driven into it, together with the water.

To avoid this, the combustion tube was drawn out in two places so as to form a kind of bulb in which all the mercury and the greater part of the water condensed. The chloride of calcium tube was attached in the usual manner beyond the bulb.

After the combustion was completed, all that portion of the combustion tube which projected from the furnace was cut off by means of a file at one of the narrow necks; the chloride of calcium tube remaining attached to it. The water was then swept into the chloride of calcium tube by means of a current of dry air drawn through by an aspirator. The mercury was dissolved and determined as sulphide.

Details of analyses of the first salt :

CHROMIC ACID DETERMINATIONS BY IGNITION.

- I. 0.210 grm. of the salt gave 0.0614 grm. of sesquioxide of chromium.  
 II. 0.2205 „ „ 0.0645 „ „  
 III. 0.2155 „ „ 0.0634 „ „

DETERMINATIONS OF MERCURY AND CHROMIC ACID.

- IV. 0.2565 grm. of the salt gave 0.1085 grm. of protosulphide of mercury and 0.0762 grm. of sesquioxide of chromium.  
 V. 0.434 grm. of the salt gave 0.183 grm. of protosulphide of mercury and 0.1267 grm. of sesquioxide of chromium.  
 VI. 0.2243 grm. of the salt gave 0.0940 grm. of protosulphide of mercury.

DETERMINATION OF HYDROGEN AND MERCURY.

- VII. 0.6390 grm. of the salt gave 0.1080 grm. of water (mercury lost.)  
 VIII. 0.6440 „ „ 0.1060 „ „ and 0.2720 grm. of protosulphide of mercury.

The following are the percentages calculated from these analyses :

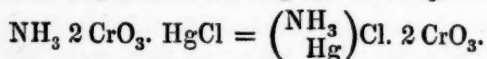
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Chromic acid	38.00	38.00	38.19	38.08	37.9	—	—	—
Mercury . .	—	—	—	36.49	36.36	36.20	—	36.40
Hydrogen .	—	—	—	—	—	—	1.87	1.83

We had not anticipated the presence of more than one equivalent of water in this substance, and it was on this account that we repeated the determinations of the various constituents several times.

The formulæ  $\text{NH}_4\text{O} \cdot 2 \text{CrO}_3 \cdot \text{HgCl}$ ,  
 and  $\text{NH}_3 \cdot 2 \text{CrO}_3 \cdot \text{HgCl}$ ,

appeared at the first glance to be the most probable; the former as an ordinary double salt of the bichromate of oxide of ammonium with protochloride of mercury, corresponding to the potassa-salt, to which Millon has assigned the formula  $\text{KO} \cdot 2 \text{CrO}_3 \cdot \text{HgCl}$ , the latter as representing a compound analogous to the bichromate of chloride of potassium, containing, in the place of potassium, the hypothetical metal mercurammonium.

The formula of the potassa-salt being  $\text{KCl} \cdot 2 \text{CrO}_3$ , we should have :



The comparison, however, of the percentages deduced from our analyses, with those calculated from the preceding formulæ, and



from the formula  $\text{NH}_4\text{O} \cdot 2 \text{CrO}_3 \cdot \text{HgCl} + \text{HO}$ , leave no doubt that the latter is the constitution of the salt as we obtained it.

	$\text{NH}_4\text{O} \cdot 2 \text{CrO}_3 \cdot \text{HgCl}$	$\text{NH}_3 \cdot 2 \text{CrO}_3 \cdot \text{HgCl}$	$\text{NH}_4\text{O} \cdot 2 \text{CrO}_3 \cdot \text{HgCl} + \text{HO}$
Chromic acid . . .	39·24	40·61	37·96
Mercury . . .	37·62	38·94	36·39
Chlorine . . .	13·35	13·83	12·92
Nitrogen . . .	5·27	5·45	5·09
Hydrogen . . .	1·51	1·17	1·82
Oxygen (as water) . .	3·01	—	5·82
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

The product of the second crystallization proved to be identical with the preceding.

I. 0·4215 grm. of salt gave 0·1215 grm. of sesquioxide of chromium corresponding to 37·94 per cent of chromic acid.

II. 0·463 grm. of salt gave 0·1954 of protosulphide of mercury, corresponding to 36·39 per cent of mercury, and 0·1354 grm. of sesquioxide of chromium, corresponding to 37·97 per cent of chromic acid.

Another specimen of the salt was prepared which yielded the same results.

Lastly, the product of the third crystallization was analysed and yielded the following numbers:

I. 0·1880 grm. of salt gave 0·0862 grm. of sesquioxide of chromium			
II. 0·2093   "   "   "   "   "   "	0·0958	"	"
III. 0·2068   "   "   "   "   "   "	0·0454	"	protosulphide of mercury
IV. 0·2190   "   "   "   "   "   "	0·0480	"	"

Calculated percentages:

	I.	II.	III.	IV.
Chromic acid . . .	59·52	59·43	—	—
Mercury . . .	—	—	18·91	18·90

Theoretical percentages for the formula  $3(\text{NH}_4\text{O} \cdot 2 \text{CrO}_3) \cdot \text{HgCl}$ :

Chromic acid . . . . .	59·44
Mercury . . . . .	18·99
Ammonia . . . . .	9·69
Water . . . . .	5·13
Chlorine . . . . .	6·75

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100·00

It will be seen that the calculated percentages agree very closely with those required by this formula.

June 17, 1850.

THOMAS GRAHAM, Esq., V.P., in the Chair.

John Bennett Lawes, Esq. and Frederick Vaux, Esq. were elected Fellows of the Society.

The following presents were announced :

"Proceedings of the American Philosophical Society," No. 44 : presented by the Society.

"On a New Medium for Mounting Organic Substances as Permanent Objects for Microscopic Inspection," by Robert Warington: presented by the Author.

The following papers were read :

## XXII.—Description of an Ammonia-Meter.

BY JOHN JOSEPH GRIFFIN, F.C.S.

I take the liberty of presenting to the Chemical Society a Hydrometer for determining the strength of solutions of Ammonia. I think it may be interesting to the Society, because it is founded on a chemical principle, while its indications are such as adapt it to the use of the manufacturer.

In a memoir which the Society did me the honour to insert in their Transactions four years ago,\* I recited some experiments to prove, that mixtures of liquid ammonia with water possess a specific gravity which is the mean of the specific gravities of their components ; that



in all solutions of ammonia, a quantity of anhydrous ammonia, weighing  $212\frac{1}{2}$  grains, which I call a *Test-atom*, displaces 300 grains of water, and reduces the specific gravity of the solution to the extent of .00125; and finally, that the strongest solution of ammonia which it is possible to prepare at the temperature of  $62^{\circ}$  Fah. contains in an imperial gallon of solution, one hundred test-atoms of ammonia. The new Ammonia-Meter is founded upon those facts.

The form of the instrument is that of an ordinary glass hydrometer, with a paper scale showing 100 degrees. Every degree indicates 1 test-atom, or  $212\frac{1}{2}$  grains, of anhydrous ammonia, in the gallon of solution. The zero of the scale signifies pure water at the temperature of  $62^{\circ}$  F.

\* On the Constitution of Aqueous Solutions of Acids and Alkalies. Mem. Chem. Soc. III, 188.

The first degree signifies 1 test-atom of ammonia, and the hundredth degree 100 test-atoms. The specific gravity of the liquor which corresponds with 100° of strength is .875, water being taken at 1.000.

To render the indications afforded by this instrument useful to manufacturers, I have prepared a table which shows the constitution of the hundred solutions of ammonia corresponding with the hundred degrees of the instrument. The table contains six columns of numbers. The first column shows the *specific gravity* of the solutions; the second column, the *weight* of an imperial gallon in avoirdupois pounds and ounces; the third, the *percentage* of ammonia by weight; the fourth column, the *degree* of the solution as indicated by the instrument, corresponding with the number of *test-atoms* of ammonia present in a gallon of the liquor; the fifth column shows the number of *grains* of ammonia contained in a gallon; and the sixth column, the *atomic volume* of the solution, or that *measure* of it which contains one test-atom of ammonia. The horizontal lines represent the various equivalents of every degree of ammonia indicated by the instrument.

The Ammonia-Meter and the Table together will enable a manufacturer to determine, not only the actual strength of any given liquor, but the precise amount of dilution necessary to convert it into a liquor of any other desired strength. Thus, a liquor indicating 96° by this instrument has a specific gravity of .88, and another indicating 32° has a specific gravity of .96. If the strong liquor is to be diluted to form the weak liquor, the numbers in column 6 of the table show, that 104.16 measures of the former must be diluted to 312.5 measures of the latter.

The direct quotation of the number of grains of ammonia contained in a gallon of solution, enables one to judge at a glance of the money value of any given sample of ammonia. Finding that a liquor at 33° contains about one pound of ammonia; a second liquor at 66°, two pounds; and a third at 99°, three pounds, in the gallon, we perceive at once the relative value of these liquors.

The degrees of this instrument mark the strength of solutions of ammonia in a more comprehensible manner than is done by a statement of their Specific Gravities. Thus, the weak liquid ammonia of the London Pharmacopœia has a specific gravity of .96, and that of the Dublin Pharmacopœia a specific gravity of .95. A gallon of the latter weighs only  $1\frac{6}{10}$  ounce less than a gallon of the former. These comparisons do not appear to indicate any great difference in the strength of the liquors; yet the new Ammonia-Meter marks the London ammonia as of 32° and the Dublin ammonia as of 40°; and

the respective strengths of the liquors agree with these numbers, the Dublin solution containing 25 per cent more ammonia than the London solution.

In proposing to determine the strength of solutions of ammonia by a hydrometric process, I do so in accordance with the practice of chemical manufacturers; but I may add, that, in point of accuracy, the best hydrometer that can be made, stands, for such a purpose, far behind the chemical process of centigrade testing. This arises from the fact, that the density of ammonia in solution closely approximates to the density of water. A gallon of water weighs only 20 ounces more than a gallon of the strongest solution of ammonia. The extreme difference between the specific gravities of the two liquids is only  $\cdot 125$ . Every degree of the Ammonia-Meter shows the hundredth part of that difference, and therefore indicates an alteration equal to  $\frac{1}{2}$  of an ounce in 10 lbs. of water, or the 800th part of the entire weight. As a hydrometer of many spindles is expensive and troublesome, and as a single spindle cannot conveniently carry above 100 degrees, this instrument may be said to exhaust the capabilities of such a mode of trial;—but, centigrade testing, applied to ammonia, readily discriminates ten degrees of chemical strength between each of the hydrometric degrees.

The following precautions are necessary to be taken in using the Ammonia-Meter :

1. The instrument must not be warmed by the hand before insertion into the liquor to be tried.—2. The spindle must not be unnecessarily wetted by the liquor : to prevent this, the instrument in a dry state should be put gently into the liquor, and the jar or table be tapped till the hydrometer sinks to the proper level.—3. The lines on the scale are drawn level with the general surface of the liquor under trial, not with the liquor which capillary attraction draws up round the spindle.—4. It must be borne in mind, that when the solution of Ammonia has been made with undistilled water, the apparent strength will be *less* than the real strength, according to the increase of density due to the impurities contained in the water.\*

\* The specific gravity of the Thames water at Greenwich is 1·00116, (Bennett, Chem. Soc. Qu. J. II, 109), and that of London Well-water is 1·0007, (Brande, *ibid*, II, 349). Liquid ammonia prepared with the former would be 1°, with the latter,  $\frac{1}{4}$ ° stronger than the degree indicated by the instrument.

## TABLE OF LIQUID AMMONIA.

One Test-Atom of Anhydrous Ammonia =  $\text{NH}_3$  weighs 212.5 grains.

Sp. Gr. of Water = 1.00000. One Gallon of Water weighs 10 lbs. and contains 10,000 Septems. Temperature 62° Fahr.

Specific gravity of the liquid ammonia.	Weight of an imperial gallon in avoirdupois lbs. and ozs.	Percentage of ammonia by weight.	Test-atoms of ammonia in one gallon.	Grains of ammonia in one gallon.	Septems containing 1 test-atom of ammonia.	Specific gravity of the liquid ammonia.	Weight of an imperial gallon in avoirdupois lbs. and ozs.	Percentage of ammonia by weight.	Test-atoms of ammonia in one gallon.	Grains of ammonia in one gallon.	Septems containing 1 test-atom of ammonia.	Specific gravity of the liquid ammonia.	Weight of an imperial gallon in avoirdupois lbs. and ozs.	Percentage of ammonia by weight.	Test-atoms of ammonia in one gallon.	Grains of ammonia in one gallon.	Septems containing 1 test-atom of ammonia.	Specific gravity of the liquid ammonia.	Weight of an imperial gallon in avoirdupois lbs. and ozs.	Percentage of ammonia by weight.	Test-atoms of ammonia in one gallon.	Grains of ammonia in one gallon.	Septems containing 1 test-atom of ammonia.	
87500	8 lb. 12 <sup>1</sup> / <sub>2</sub> oz.	34.694	100	21250.9	100.00	91750	9 lb. 2 <sup>1</sup> / <sub>2</sub> oz.	21.837	66	14025.0	151.51	95875	9 lb. 9 <sup>1</sup> / <sub>2</sub> oz.	10.4490	33	7012.5	308.03							
87625	8 .. 12 ..	34.298	99	21037.5	101.01	91575	9 .. 3 ..	21.477	65	13812.5	153.85	96000	9 .. 9 <sup>1</sup> / <sub>2</sub> ..	10.1190	32	6900.0	312.50							
87750	8 .. 12 ..	33.903	98	20850.0	102.04	91400	9 .. 3 ..	21.118	64	13600.0	156.25	96125	9 .. 9 ..	9.7901	31	6587.5	322.58							
87875	8 .. 12 ..	33.509	97	20662.5	103.09	91225	9 .. 3 ..	20.760	63	13387.5	158.75	96250	9 .. 10 ..	9.4620	30	6275.0	333.33							
88000	8 .. 12 ..	33.117	96	20475.0	104.16	91050	9 .. 3 ..	20.403	62	13175.0	161.29	96375	9 .. 10 ..	9.1347	29	6162.5	344.83							
88125	8 .. 13 ..	32.725	95	20287.5	105.26	90875	9 .. 3 ..	20.046	61	12962.5	163.93	96500	9 .. 10 ..	8.8347	28	5950.0	356.34							
88250	8 .. 13 ..	32.335	94	20100.0	106.38	90700	9 .. 4 ..	19.691	60	12750.0	166.67	96625	9 .. 10 ..	8.5087	27	5737.5	367.87							
88375	8 .. 13 ..	31.946	93	19912.5	107.53	90525	9 .. 4 ..	19.332	59	12537.5	169.49	96750	9 .. 10 ..	8.1880	26	5525.0	379.37							
88500	8 .. 13 ..	31.558	92	19725.0	108.70	90350	9 .. 4 ..	18.983	58	12325.0	172.41	96875	9 .. 10 ..	7.8841	25	5312.5	390.87							
88625	8 .. 13 ..	31.172	91	19537.5	109.89	90175	9 .. 4 ..	18.631	57	12112.5	175.44	97000	9 .. 11 ..	7.5811	24	5100.0	402.37							
88750	8 .. 14 ..	30.745	90	19350.0	111.11	89999	9 .. 4 ..	18.280	56	11900.0	178.57	97125	9 .. 11 ..	7.2799	23	4887.5	413.87							
88875	8 .. 14 ..	30.360	89	19162.5	112.36	89825	9 .. 5 ..	17.929	55	11687.5	181.82	97250	9 .. 11 ..	6.9875	22	4675.0	425.37							
89000	8 .. 14 ..	30.016	88	18975.0	113.64	89650	9 .. 5 ..	17.579	54	11475.0	185.18	97375	9 .. 11 ..	6.6469	21	4462.5	436.87							
89125	8 .. 14 ..	29.633	87	18787.5	114.94	89475	9 .. 5 ..	17.231	53	11262.5	188.68	97500	9 .. 12 ..	6.3271	20	4250.0	448.37							
89250	8 .. 14 ..	29.252	86	18599.9	116.28	89300	9 .. 5 ..	16.883	52	11050.0	192.31	97625	9 .. 12 ..	5.9932	19	4037.5	459.87							
89375	8 .. 15 ..	28.871	85	18412.5	117.65	89125	9 .. 5 ..	16.536	51	10837.5	196.08	97750	9 .. 12 ..	5.5901	18	3825.0	471.37							
89500	8 .. 15 ..	28.492	84	18225.0	119.05	88950	9 .. 6 ..	16.190	50	10625.0	200.00	97875	9 .. 12 ..	5.2728	17	3612.5	482.87							
89625	8 .. 15 ..	28.113	83	18037.5	120.48	88775	9 .. 6 ..	15.846	49	10412.5	204.08	98000	9 .. 12 ..	4.9533	16	3400.0	494.37							
89750	8 .. 15 ..	27.736	82	17850.0	121.95	88600	9 .. 6 ..	15.502	48	10200.0	208.33	98125	9 .. 13 ..	4.6006	15	3187.5	505.87							
89875	8 .. 15 ..	27.359	81	17662.5	123.46	88425	9 .. 6 ..	15.158	47	9987.5	212.77	98250	9 .. 13 ..	4.2525	14	2975.0	517.37							
89900	9 .. 0 ..	26.984	80	17475.0	125.00	88250	9 .. 6 ..	14.816	46	9775.0	217.33	98375	9 .. 13 ..	3.9041	13	2762.5	528.87							
90025	9 .. 0 ..	26.610	79	17287.5	126.58	88075	9 .. 7 ..	14.473	45	9562.5	222.22	98500	9 .. 13 ..	3.5568	12	2550.0	540.37							
90150	9 .. 0 ..	26.237	78	17100.0	128.21	87900	9 .. 7 ..	14.130	44	9350.0	227.27	98625	9 .. 13 ..	3.2095	11	2337.5	551.87							
90275	9 .. 0 ..	25.865	77	16912.5	129.87	87725	9 .. 7 ..	13.785	43	9137.5	232.36	98750	9 .. 14 ..	2.8622	10	2125.0	563.33							
90375	9 .. 0 ..	25.493	76	16725.0	131.58	87550	9 .. 7 ..	13.443	42	8925.0	237.69	98875	9 .. 14 ..	2.5148	9	1912.5	574.87							
90500	9 .. 1 ..	25.123	75	16537.5	133.33	87375	9 .. 7 ..	13.100	41	8712.5	243.90	99000	9 .. 14 ..	2.1673	8	1700.0	586.33							
90625	9 .. 1 ..	24.754	74	16350.0	135.13	87200	9 .. 8 ..	12.758	40	8500.0	250.00	99125	9 .. 14 ..	1.8200	7	1487.5	597.87							
90750	9 .. 1 ..	24.386	73	16162.5	136.98	87025	9 .. 8 ..	12.416	39	8287.5	256.41	99250	9 .. 14 ..	1.4724	6	1275.0	609.37							
90875	9 .. 1 ..	24.019	72	15975.0	138.89	86850	9 .. 8 ..	12.073	38	8075.0	263.16	99375	9 .. 15 ..	1.1250	5	1062.5	620.87							
91000	9 .. 1 ..	23.653	71	15787.5	140.85	86675	9 .. 8 ..	11.731	37	7862.5	270.27	99500	9 .. 15 ..	0.7774	4	850.0	632.33							
91125	9 .. 2 ..	23.288	70	15599.9	142.86	86500	9 .. 8 ..	11.388	36	7650.0	277.78	99625	9 .. 15 ..	0.4300	3	637.5	643.87							
91250	9 .. 2 ..	22.924	69	15412.5	144.93	86325	9 .. 9 ..	11.045	35	7437.5	285.71	99750	9 .. 15 ..	0.0827	2	425.0	655.33							
91375	9 .. 2 ..	22.561	68	15225.0	147.06	86150	9 .. 9 ..	10.702	34	7225.0	294.12	99875	9 .. 15 ..	0.0000	1	212.5	666.87							
91500	9 .. 2 ..	22.198	67	15037.5	149.25	85975	9 .. 9 ..	10.359	33	7012.5	302.63	99900	9 .. 15 ..	0.0000	0	100.0	678.33							
91625	9 .. 2 ..	21.837	66	14850.0	151.48	85800	9 .. 9 ..	10.016	32	6800.0	311.13	100000	9 .. 15 ..	0.0000	0	100.0	689.87							

Water.

10 lbs.

1.0000

1.

6.

5.

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XXIII.—*Contributions towards the history of Caproic and Enanthylic Acids.*

BY MESSRS. J. S. BRAZIER AND G. GOSSLETH,

*Of the Royal College of Chemistry, London.*

The leading notions, which begin to elucidate the vast number of observations collected in the department of organic chemistry, have been acquired in the careful study of a comparatively limited number of groups of analogous substances. The investigation of a series of bodies closely allied to each other in their composition and properties, and a comparison of their composition and properties, imparted to the results obtained a degree of interest, which could not have been possibly claimed by the most accurate and minute examination of an isolated compound.

Among the groups of substances, the study of which has thus most materially assisted in the elaboration of our theoretical views, the series of acids, usually called fatty acids, appears in the first rank. This series, commencing with formic acid, the simplest of all organic acids, and terminating with an acid of so high an equivalent as melissic acid, discovered by Mr. Brodie,\* is at once distinguished by the definite character of its members, by the extent to which it is represented by well-investigated terms, and by the variety of sources, belonging to almost all the various departments of organic chemistry from which these terms have been derived. Descending from the alcohols by way of the aldehydes, and connected with the former group in another manner by the nitriles, again related in its derivatives with marsh-gas and its homologues, as well as with the increasing family of acetones, the history of this group, when traced in its various ramifications, extends over a field on which we meet with almost all the compounds essentially concerned in the progress of chemical science.

In the following pages, we beg to communicate to the Society, a few contributions towards the history of the fatty acids, which, notwithstanding their fragmentary nature, may be acceptable on account of the interest attached to the subject. These communications refer to the sixth and seventh term of the series of fatty acids, namely caproic and enanthylic acids.

CAPROIC ACID.

This acid, discovered by Chevreul in the course of his forgotten researches into the nature of fatty bodies, and subsequently met with



in cocoa-nut oil by Fehling,\* has been produced of late under very remarkable circumstances from cyanide of amyl, by Messrs. Kolbe and Frankland.† In order to avoid the tedious processes of saponification, and subsequent fractional distillation of the volatile products, or of separating the acids by the different solubility of their baryta-salts, we resolved to prepare the acid by the latter method. In the course of this process, we made one or two observations which may be mentioned.

The sulphamylate of potassa, used in making cyanide of amyl, was prepared at once from sulphamylic acid, by saturating it with crude carbonate of potassa. Nearly the whole of the excess of sulphate of potassa formed was separated during this operation, the remaining portion crystallizing out by the evaporation of the solution.

The perfectly dry sulphamylate of potassa, when distilled with cyanide of potassium in the proportion of three to one, yields cyanide of amyl. In the commencement we performed this distillation on a rather considerable scale in iron retorts: the irregular action of the heat, however, induced the formation of a large amount of secondary products; and we found it more advisable to work with smaller portions. The operation succeeds very well in Florence flasks, placed obliquely upon a wire-gauze over a gas-burner. The liquid obtained in this distillation is by no means a definite compound. Its terrible odour indicates at once the presence of a considerable amount of prussic acid. When subjected to distillation, it begins to boil at about  $125^{\circ}\text{C}$ . ( $257^{\circ}\text{F}$ .), the boiling-point rising gradually to  $150^{\circ}\text{C}$ . ( $302^{\circ}\text{F}$ .), about which temperature, a semi-solid, yellowish-white mass, of crystalline appearance, remains behind in the retort. A similar product is deposited in the tube of the condenser. It may here at once be stated that this liquid contains, in addition to cyanide of amyl, a good deal of fusel-oil, and moreover a considerable quantity of both liquid cyanate and solid cyanurate of amyl, the two latter evidently arising from the presence of a large amount of cyanate of potassa in the commercial cyanide of potassium. This substance, which is now manufactured in this country by hundred-weights, is invariably prepared by Liebig's process, the success of which, as is well known, actually depends upon the simultaneous formation of the cyanate.

In the first place, we attempted to purify the crude cyanide previously to its conversion into caproic acid; but after having ascertained

\* Ann. Ch. Pharm. LIII, 390.

† Ann. Ch. Pharm., LXIX, 418.

the nature of the impurities, we at once subjected the crude product collected between  $130^{\circ}$  and  $150^{\circ}$  to the action of the alkali. The products of decomposition furnished by the cyanide and cyanate are so opposite in their chemical character—the one yielding a strong acid caproic acid, the other a powerful base—amylamine or valeramine—while the fusel-oil present remains unaltered—that the separation after decomposition follows as a matter of course, whilst separation, by fractional distillation before the action, would have been a tedious and nevertheless imperfect operation.

The conversion of the cyanide of amyl may be effected by an aqueous solution of potassa: we found, however, that the operation succeeds much better with a solution of the alkali in alcohol. The mixture, when boiled in a flask connected with a condenser in such a manner as to induce the liquid to return to the alkali, readily changes into a pasty mass, while torrents of ammonia are evolved. After half an hour's ebullition, the mixture is introduced into a retort and subjected to distillation, when a small quantity of ammonia, alcohol, amylamine, and fusel-oil distil over, a solution of caproate of potassa remaining behind, which usually solidifies on cooling into a semi-crystalline mass.

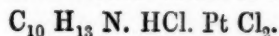
The distillate was mixed with some hydrochloric acid, and subjected once more to distillation; it began to boil at about  $78^{\circ}$  C. ( $172^{\circ}\cdot4$  F.), the first product consisting of alcohol; the boiling-point rose gradually to  $131^{\circ}$  C. ( $267^{\circ}\cdot8$  F.), at which temperature pure fusel-oil distilled over, a syrupy mass remaining behind, containing chiefly hydrochlorate of amylamine, and from which an additional quantity of fusel-oil was separated by addition of water. The dilute solution, when boiled for some time, in order to drive off fusel-oil, which was still mechanically adhering, and distilled with potassa, yielded a considerable quantity of pure amylamine. The production of this base under these circumstances is, as we have mentioned, due to the decomposition of the cyanate and cyanurate of amyl: these substances, as Wurtz has shown, assimilating the elements of water, are split up into carbonic acid and amylamine. In several operations, the production of the latter base nearly equalled the quantity of caproic acid obtained, which shows how much cyanate is present in many kinds of commercial cyanide of potassium. With respect to the properties of amylamine, we have scarcely to add anything to Wurtz's description; however, as we had a considerable quantity of the substance at our disposal, we determined its boiling-point with accuracy. Amylamine boils constantly at  $93^{\circ}$  C. ( $199^{\circ}\cdot4$  F.) We adduce, moreover, an analysis of the platinum-

salt of this base, which leaves no doubt as to its identity with amylamine.

The platinum-salt, being soluble in water, was easily purified by one or two recrystallizations.

- I. 0.5722 grms. of platinum-salt gave:  
 0.4259 " " carbonic acid, and  
 0.2578 " " water.  
 II. 0.6210 " " platinum-salt gave:  
 0.2077 " " platinum.

These numbers lead to the following percentage, which we place in juxtaposition with the theoretical values of the formula,



		Theory.		Experiment.
10 eqs. of Carbon	. . .	60.00	20.46	20.30
14 " " Hydrogen	. .	14.00	4.78	5.00
1 " " Nitrogen	. .	14.00	4.78	—
3 " " Chlorine	. . .	106.50	36.33	—
1 " " Platinum	. .	98.68	33.65	33.45
1 eq. of Bichloride of Platinum and Amylamine }		293.18	100.00	—

The solution of caproate of potassa, concentrated if requisite by evaporation, was gradually mixed with sulphuric acid, when caproic acid separated as an oily liquid, lighter than water. It was removed by a tap-funnel, and subjected to rectification.

The acid obtained in this manner was not perfectly pure; when submitted to distillation, it was found that the thermometer rose at once to, and became constant at,  $198^{\circ} \text{C.}$  ( $388^{\circ} \cdot 4 \text{ F.}$ ); at which temperature, the larger portion of the fluid distilled over; the mercury then rose gradually to  $211^{\circ} \text{C.}$  ( $411^{\circ} \cdot 8 \text{ F.}$ ) The first fraction, when rectified, exhibited exactly the same boiling-point as before, several ounces distilling over without any oscillation of the mercury, whence we do not hesitate to consider  $198^{\circ} \text{C.}$  ( $388^{\circ} \cdot 4 \text{ F.}$ ) as the boiling-point of caproic acid: Fehling\* had found that the acid obtained from cocoa-nut oil boiled at  $202^{\circ} \text{C.}$  ( $395^{\circ} \cdot 6 \text{ F.}$ )

#### CAPROATE OF AMYL.

We have just stated that the thermometer continued to rise after the distillation of the pure acid. The product, passing over between

\* Ann. Ch. Pharm. LIII, 390.

200° and 211°, differed in its odour from that of caproic acid; it was found to be partly soluble in alkaline, and not at all in acid liquids, and formed only a comparatively small percentage of the total amount of liquid. In order to obtain a sufficient quantity of this compound for examination, a considerable portion of crude caproic acid was treated with a solution of carbonate of potassa, when the caproic acid was dissolved with evolution of carbonic acid, an oily liquid separating on the surface of the solution. When removed with a separating funnel and dried over chloride of calcium, it exhibited after rectification, a constant boiling-point at 211° C. (411°8 F.)

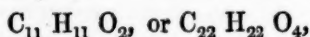
The analysis of the oily liquid gave the following results:

- I. 0.2485 grms. of substance gave :  
 0.6410 " " carbonic acid, and  
 0.2675 " " water.  
 II. 0.2075 " " substance gave :  
 0.5386 " " carbonic acid, and  
 0.2231 " " water.

Percentage-composition :

		I.	II.
Carbon	. .	70.75	70.80
Hydrogen	. .	11.95	11.94

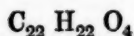
These numbers closely agree with the formula,



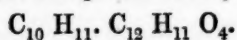
as exhibited in the following comparison of the theoretical values, with the results of experiment :

		Theory.		Mean of Experiment.
22 eqs. of Carbon	. . .	132	70.96	70.78
22 " " Hydrogen	. .	22	11.82	11.94
4 " " Oxygen	. . .	32	17.22	—
		<hr/>	<hr/>	
		186	100.00	

The formula,



represents the composition of caproate of amyl:



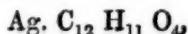
The observed boiling-point of this compound coincides pretty closely with the number calculated, if we start from the boiling-point of valerate of amyl, which, according to Balard's determination,

is 190° C. (374° F.) The deportment of the above substance with an alcoholic solution of potassa, leaves no doubt in this respect. The mixture when heated, was readily converted into a gelatinous mass, from which water separated pure fusel-oil, while addition of sulphuric acid to the remaining alkaline solution, induced the liberation of an oily acid, which by analysis was proved to be caproic acid. When it was separated by distillation, dissolved in ammonia, and converted into a silver-salt

0.2814 grms. of silver-salt gave:

0.1408 „ „ silver = 48.65 per cent. of silver.

The formula,



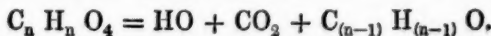
requires 48.43 per cent.

Caproate of amyl has a very disagreeable smell and pungent taste, is perfectly insoluble in water, of a lower specific gravity, but soluble in every proportion of alcohol and ether.

The formation of caproate of amyl under the adduced circumstances, appeared at the first glance rather enigmatical. We soon found, however, that fusel-oil is soluble to a certain extent in a solution of caproate of potassa. The separation of caproic acid by sulphuric acid in the presence of amyl-alcohol, could not fail to produce a certain quantity of the compound ether in question.

#### ACTION OF HEAT UPON CAPROATE OF BARYTA.

The members of the series  $\text{C}_n \text{H}_n \text{O}_4$ , when subjected to the action of heat, split, as is well known, into water, carbonic acid, and a new class of bodies known under the name of acetones or ketones, according to the following equation:



This metamorphosis is generally effected by the distillation of the lime- or baryta-salts, in which case the carbon becomes fixed in the form of a carbonate.

In preparing the ketone of caproic acid, we availed ourselves of the baryta-salt.

This salt is easily prepared by means of carbonate of baryta and caproic acid; it is very soluble in water. The solution, when left to evaporate *in vacuo* over sulphuric acid, deposits crystalline plates. By ebullition, the odour of caproic acid becomes perceptible, and a white mass separates, which can be dried without decomposition at a temperature a little above 100° C. The dry mass, evidently a

somewhat basic salt, is brittle and may be easily powdered; for the distillation of the salt we employed small quantities at a time. At a gentle heat, the salt fuses without charring in the least, nearly white carbonate of baryta remaining behind; nevertheless, only a comparatively small quantity of liquid product is obtained as distillate. Experiment showed at once that the action by no means consists exclusively in a separation of carbonic acid; for during the whole process a permanent, inflammable gas was evolved, the quantity of which appeared to increase in some measure with the temperature at which the distillation was performed. Caproate of baryta, when suddenly exposed to a rapidly rising temperature, disengages this gas in considerable quantities, only a small portion of oily products being formed, which are moreover very dark and resinous, whilst the distillate obtained at moderate temperatures is nearly colourless. The carbonate of baryta which remains in the retort is nearly black from separated carbon. These facts, as well as the observations made by Chancel and Guckelberger\* in the analogous decomposition of butyric, valeric and caprylic acids, left no doubt that the liquid product was a mixture of various substances. When dried over chloride of calcium and subjected to distillation, it commenced boiling at  $120^{\circ}\text{C}$ . ( $248^{\circ}\text{F}$ .), the boiling-point rising gradually to  $170^{\circ}\text{C}$ . ( $338^{\circ}\text{F}$ .) Between  $160^{\circ}$  and  $170^{\circ}$  the largest quantity was collected. This portion, on rectification, showed a pretty constant boiling-point at  $165^{\circ}\text{C}$ . ( $329^{\circ}\text{F}$ .) With the lower portions, no constant boiling-temperature could be observed. Several combustions made with this product, exhibited invariably a deficiency of carbon when compared with the percentage of carbon required by the formulae of caprone,  $\text{C}_{11}\text{H}_{11}\text{O}$ . This, as well as the results of Chancel, who actually separated butyral, or at all events a substance of similar composition from the product of distillation of butyrate of lime, lead us to believe that a small quantity of caprale,  $\text{C}_{12}\text{H}_{12}\text{O}_2$ , may be formed in this process.

This assumption is supported by the deportment of the lower distillate, from which ammonia removes a small portion of matter. The ammoniacal solution, after having been exposed to the air for some time, yields with acids oily globules having the characteristics of caproic acid. Unfortunately, we had not enough material to elaborate this question any further. We were, however, benefitted by the observation, inasmuch as it induced us to submit the chief fraction boiling at about  $165^{\circ}$ , previously to analysis, to an addi-

\* Ann. Ch. Pharm. LXIX, 20.



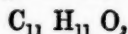
tional distillation over hydrate of potassa. After this treatment, it showed a constant-boiling point at  $165^{\circ}\text{C}$ . ( $329^{\circ}\text{F}$ .). When burnt with protoxide of copper, this liquid gave the following results:

I. 0.1641 grms. of substance gave :		
0.4655	"	" carbonic acid, and
0.1949	"	" water.
II. 0.2263 " " substance gave :		
0.6423	"	" carbonic acid, and
0.2668	"	" water.

Percentage-composition :

	I.	II.
Carbon . . .	77.36	77.42
Hydrogen . . .	13.18	13.10

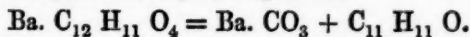
These numbers closely correspond with the formula



as may be seen from the following table:

	Theory.		Mean of Experiment.
11 eqs. of Carbon . .	66	77.64	77.39
11 " " Hydrogen . .	11	12.94	13.14
1 " " Oxygen . .	8	9.42	—
1 eq. " Caprone . .	85	100.00	

Caprone is a very mobile liquid, insoluble in water, to which however it imparts its peculiar odour; it is readily soluble in alcohol and ether. After being distilled from potassa, it is perfectly colourless, but rapidly turns brown when in contact with the atmosphere, probably in consequence of oxidation. Its boiling-point is  $165^{\circ}\text{C}$ . ( $329^{\circ}\text{F}$ .), and its specific gravity is lower than that of water. These results show that one phase of the action of heat upon caproate of baryta, may be represented by the equation :



We say one phase, because a series of other metamorphoses is proceeding simultaneously with the conversion of a portion of the acid into caprone. The amount of this substance obtained is quite out of proportion with the quantity of baryta-salt employed. We have mentioned that we have reason to believe that the aldehyde of caproic acid is simultaneously formed, and alluded to the large quantity of permanent gas disengaged. This gas consists chiefly of hydrocarbons, and probably contains a similar mixture of the hydrocarbons

$C_n H_{2n}$ , which Dr. Hofmann observed in the distillation of valerianic acid.\*

The preparation of caprone adds another member to the group of ketones running parallel with the series of fatty acids. This group, first announced in the formation of acetone, which may be still considered as its prototype, and subsequently illustrated by Chancel's researches into the derivatives of butyric and valeric acids, embraces at this moment the following members, which we give in juxtaposition with their mother-acids :

Acetic acid	. . $C_4 H_4 O_4$ ;	$C_3 H_3 O$ ,	Acetone;	Liebig & Dumas.
Propionic acid . }	$C_6 H_6 O_4$ ;	$C_5 H_5 O$ ,	{ Propione;	Frémy.
Metacetic acid . }			{ Metacetone;	
Butyric acid	. . $C_8 H_8 O_4$ ;	$C_7 H_7 O$ ,	Butyrone;	Chancel.
Valeric acid	. . $C_{10} H_{10} O_4$ ;	$C_9 H_9 O$ ,	Valerone;	Chancel.
Caproic acid	. . $C_{12} H_{12} O_4$ ;	$C_{11} H_{11} O$ ,	Caprone;	G. & B.
Caprylic acid	. . $C_{16} H_{16} O_4$ ;	$C_{15} H_{15} O$ ,	Caprylone;	Guckelberger.
Margaric acid	. . $C_{34} H_{34} O_4$ ;	$C_{33} H_{33} O$ ,	Margarone;	Bussy.

This table shows that the ketone of formic acid is still wanting; the series then regularly ascends up to cœnanthylic acid, whose derivative has not yet been prepared; we perceive, moreover, that a wide gap occurs between caprylic and margaric acid, the filling up of which will require some time and labour. It deserves to be mentioned that one of the terms which we have inserted in the above table, has not hitherto been obtained from the collateral acid. Propione (metacetone) originally prepared by Frémy by distilling sugar, starch, or gum, with lime, has been represented by its discoverer by the formula  $C_6 H_5 O$ ; it is probable, however, that Frémy's substance contains one equiv. of carbon less. Its properties coincide in almost every respect with propione, as pointed out by theory.

Acetone and its congeners have been of late the subject of some interesting speculations on the part of M. Chancel.† The formula which we have given in the above table, represents 2 volumes of vapour, and this is the mode of condensation adopted by the majority of chemists. M. Chancel on the other hand is of opinion, that the ketones, like the hydrocarbons, contain 4 vols. of vapour: he doubles

\* The chief component of this gas is, as I have stated, propylene. I have since learnt from M. Cahours, that pelargonic, caprylic, and cœnanthylic acids likewise yield this hydrocarbon in preponderating quantities, so that we may fairly assume that caproic acid exhibits a similar deportment.—A. W. H.

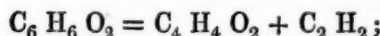
† J. Pharm. [3] XIII, 468.

the formulæ, and considers these substances as formed by the intimate combination of 1 equivalent of the aldehyde of the acid with 1 equivalent of the hydrocarbon belonging to the group which is placed a step lower on the ladder of organic substances.

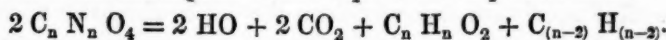
According to this view, acetone is not represented by



but by



i. e. it has to be considered as a combination of the aldehyde (*par excellence*), and methylene: consequently the ketones would always arise from the decomposition of 2 eqs. of the respective acids:



The following table, into which we introduce the boiling-points which have been observed, exhibits the various ketones when viewed in this light:

						Boiling-point.
Acetone	. $C_6$	$H_6$	$O_2 = C_4$	$H_4$	$O_2 + C_2$	$H_2 \dots 56^\circ C. (132^\circ.8 F.)$
Propione	. $C_{10}$	$H_{10}$	$O_2 = C_8$	$H_8$	$O_2 + C_4$	$H_4 \dots 84^\circ C. (183^\circ.2 F.)$
Butyrene	. $C_{14}$	$H_{14}$	$O_2 = C_{12}$	$H_{12}$	$O_2 + C_6$	$H_6 \dots 144^\circ C. (291^\circ.2 F.)$
Valerone	. $C_{18}$	$H_{18}$	$O_2 = C_{16}$	$H_{16}$	$O_2 + C_8$	$H_8 \dots 165^\circ C. (329^\circ.0 F.)$
Caprone	. $C_{22}$	$H_{22}$	$O_2 = C_{20}$	$H_{20}$	$O_2 + C_{10}$	$H_{10} \dots 178^\circ C. (352^\circ.4 F.)$
Caprylone	. $C_{30}$	$H_{30}$	$O_2 = C_{28}$	$H_{28}$	$O_2 + C_{14}$	$H_{14} \dots 178^\circ C. (352^\circ.4 F.)$
Margarone	. $C_{66}$	$H_{66}$	$O_2 = C_{64}$	$H_{64}$	$O_2 + C_{32}$	$H_{32}$

Chancel's view is chiefly supported by the deportment of some of the ketones under the influence of oxidizing agents. In fact, acetone when boiled with chromic acid, yields a mixture of acetic and formic acids, the former being (in the conception of this theory) derived from the aldehyde, while the latter is due to the presence of a term belonging to the lower series. If acetone were  $C_3 H_3 O$ , this conversion would be almost unintelligible. In the same manner, propione is converted into propionic and acetic acids. By treating butyrene with nitric acid, Chancel\* obtains nitropropionic acid, which may have been formed by the oxidation of the propylene; Chancel gives no account of what becomes of the other term, the butaldehyde occurring in his formula. On the other hand, we find that the formation of butyrene is invariably attended by a simultaneous production of butaldehyde (butyrale), which may be due to a partial decomposition of the butyrene in the nascent state, probably with evolution of propylene. The generation of valerone and, as we have seen, of caprone, gives rise

\* J. Pharm. [3] XIII, 463.

to similar phenomena. It remained now to study the deportment of the latter compound under the influence of oxidizing agents.

#### ACTION OF NITRIC ACID UPON CAPRONE.

This body was very readily attacked by nitric acid. If strong acid was employed, oxidation ensued, without the application of heat: as soon as the evolution of nitrous fumes had ceased, the liquid in the retort was saturated with carbonate of potassa, when an oily liquid of a peculiar aromatic odour separated, which was insoluble in an excess of the alkaline liquid. The quantity at our disposal was so very small, as to preclude altogether the possibility of a closer examination.

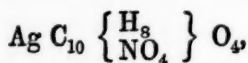
The alkaline solution separated from the oil by ebullition was now acidified with sulphuric acid, and subjected to distillation, when an acid liquid was obtained upon which a small quantity of an acid oil was floating. When saturated with ammonia and precipitated with nitrate of silver, a white crystalline silver-salt was obtained. The quantity of material at our disposal was just sufficient for a silver-determination.

0.4566 grms. of silver-salt gave:

0.1088 „ „ silver.

Percentage of silver 42.24.

This number, although somewhat low, would indicate that the salt analysed was nitrovalerate of silver; the slight deflagration which occurred on igniting the salt, gives further evidence in favour of this view. The formula,



requires 42.5 of silver.

If the acid formed by the action of nitric acid upon caprone be actually nitrovaleric acid—which has to be proved by additional experimental evidence—the deportment of this ketone would be perfectly analogous to that of butyrone, which yields nitropropionic acid. In both cases, we may ask what becomes of the aldehydes, which, according to the analogy of the lower terms, should be converted into their correlative acids, namely into caproic and butyric acids. These acids which, according to Chancel's formula, should be formed in quantities equal to those of nitrovaleric and nitropropionic acid, and which should be produced even more readily than the latter acids, have not as yet been observed in the respective processes. Hence it appears that many further researches are requisite

in order to establish Chancel's interesting speculations. The chief difficulty which we meet in the study of the higher terms of this series, is the great amount of acid required, the preparation of which is both laborious and expensive.

Before leaving this question, we may still take a glance at the boiling-point of the substance under consideration. The difference of the boiling-point of acetone and butyrene  $144^{\circ} - 56^{\circ} = 88 = 4 \times 22$ , agrees very well with Chancel's view; the boiling-point of propione is stated at  $84^{\circ}$  instead of  $100^{\circ}$ , which would be the temperature assigned by theory. However, as propione has never been prepared from propionic acid, we can scarcely place implicit reliance upon the statements at present in our possession; it is possible that the product investigated, produced as it was in an irregular process of destructive distillation, still contained some of the substances simultaneously generated, acetone, &c.

The boiling-points of caprone and caprylone (Guckelberger) are not at all favourable to Chancel's assumption. Caprone boiling at  $165^{\circ}$  C. ( $329^{\circ}$ ·0 F.), should, according to theory, boil as high as  $232^{\circ}$  C. ( $499^{\circ}$ ·6 F.); caprylone, the theoretical boiling-point of which is  $320^{\circ}$ , has been found to enter into ebullition at as low a temperature as  $178^{\circ}$  C. ( $352^{\circ}$ ·4 F.). We have, however, to bear in mind that the present state of our knowledge respecting boiling-points is very deficient; the empirical rule at which we have arrived holds good only for a certain range of the thermometer, the difference of the boiling-temperatures increasing towards the lower and decreasing towards the upper limit.

We have to apologize for the unsatisfactory state in which we are obliged to leave this question for the present: we say for the present, because it is our intention to return to this subject as soon as possible. We hope more especially soon to obtain additional data respecting the composition and the properties of nitrovaleric acid. The deportment of this acid under the influence of reducing agents promises interesting results; for should this acid — as we have every reason to believe — imitate the behaviour of nitrobenzoic acid,\* its analogue in the benzoyl-series, it will put us in possession of carbobutylic acid, from which a single step downward would lead to butylamine.

* Benzoic acid . . .	$C_{14}$	$H_6$	$O_4$	Valeric acid . . . . .	$C_{10}$	$H_{10}$	$O_4$
Nitrobenzoic acid .	$C_{14}$	$\left\{ \begin{smallmatrix} H_5 \\ NO_4 \end{smallmatrix} \right\}$	$O_4$	Nitrovaleric acid . . . . .	$C_{10}$	$\left\{ \begin{smallmatrix} H_9 \\ NO_4 \end{smallmatrix} \right\}$	$O_4$
Carbanilic acid . . .	$C_{14}$	$\left\{ \begin{smallmatrix} H_6 \\ NH_2 \end{smallmatrix} \right\}$	$O_4$	Carbobutylic acid . . . . .	$C_{10}$	$\left\{ \begin{smallmatrix} H_9 \\ NH_2 \end{smallmatrix} \right\}$	$O_4$
Aniline . . . . .	$C_{12}$	$H_7$	N	Butylamine (Petanine) . . . . .	$C_8$	$H_{11}$	N

DECOMPOSITION OF CAPROIC ACID UNDER THE INFLUENCE OF  
THE GALVANIC CURRENT.

Among the various derivatives of the series  $C_n H_n O_2$ , few have created more interest than the substances which Dr. Kolbe\* has obtained in the electrolysis of acetic, butyric, and valeric acids. In subjecting the potassa-salts of these acids to the current, he formed, among other products, the compounds:

Methyl	.	.	$C_2 H_3$
Propyl	.	.	$C_6 H_7$
Butyl (Valyl)	.	.	$C_8 H_9$

which he considers as the radicals of methylic, propylic, and butylic (valylic) alcohols. Several analogous substances, such as ethyl and amyl, having lately been obtained by Dr. Frankland† in a totally different mode of decomposition from actual alcohol-compounds, it appeared of some interest to extend the galvanic process to a case which would yield a product previously formed by the chemical method. For this purpose, we have studied the action of the pile upon caproic acid, whose decomposition promised to furnish the compound amyl,  $C_{10} H_{11}$ , previously obtained by Dr. Frankland† from iodide of amyl.

The apparatus used in the decomposition of caproate of potassa, prepared from pure caproic acid boiling at  $198^{\circ}$ , was perfectly similar to that minutely described in Dr. Kolbe's memoir. When six of Bunsen's zinco-carbon elements were employed, the decomposition of the concentrated solution of caproate of potassa succeeded without difficulty. The liquid rapidly assumed a milky appearance from the separation of numerous gas bubbles and small oily droplets, which gradually collected as a layer of oil upon the surface of the liquid contained in the decomposition-apparatus.

The gases disengaged consisted chiefly of carbonic acid and hydrogen, mixed however with a compound imparting to them a peculiar aromatic odour.

The oily liquid, when separated by means of a pipette and subjected to distillation, began to boil between  $125^{\circ} C.$  ( $257^{\circ} F.$ ) and  $160^{\circ} C.$  ( $320^{\circ} F.$ ) It was evident that, as was the case in the corresponding decomposition of valeric acid, this liquid consisted of a variety of products. Only a limited quantity being at our disposal, we at once resorted to the process of purification pointed out by Dr. Kolbe.

\* Chem. Soc. Mem. III, 373.

† Chem. Soc. Qu. J. III, 262.

‡ Chem. Soc. Qu. J. III, 30.



For this purpose the liquid was distilled with an alcoholic solution of potassa, when a potassa-salt remained in the retort, which, on addition of a mineral acid, yielded an oily acid. Although we have not made an analysis of this substance, we have no doubt that it was caproic acid; we may here adduce the analogous formation of the acids, both in the valeric, as stated by Dr. Kolbe, and in the cenanthylic series, as proved by our own experiments, detailed hereafter.

The alcoholic distillate yielded with water a light aromatic liquid, which was separated by a tap-funnel, and dried over chloride of calcium. When subjected to ebullition, it commenced boiling at  $150^{\circ}\text{C}$ . ( $302^{\circ}\text{F}$ .), the boiling-point becoming stationary at  $155^{\circ}\text{C}$ . ( $311^{\circ}\text{F}$ .), when a fraction was collected separately. At  $160^{\circ}\text{C}$ . ( $320^{\circ}\text{F}$ .), every drop had passed over.

The liquid distilling at  $155^{\circ}$  possessed all the properties assigned by Frankland to the compound obtained in the decomposition of iodide of amyl by metallic zinc.

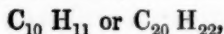
When subjected to combustion with protoxide of copper, the following numbers were obtained :

I.	0.1996	grms. of substance gave :
	0.6171	„ „ carbonic acid,*
II.	0.2130	„ „ substance gave :
	0.6579	„ „ carbonic acid, and
	0.3010	„ „ water.

Percentage-composition:

	I.	II.
Carbon . .	84.32	84.23
Hydrogen . .	—	15.70

These numbers correspond closely with the formulæ:



as may be seen from the following comparison:

	Theory.		Mean of Experiment.
10 eqs. of Carbon . .	60	84.50	84.26
11 „ „ Hydrogen . .	11	15.50	15.70
1 eq. „ Amyl . . .	71	100.00	99.96

These results leave no doubt that the substances obtained in the electrolysis of caproic acid and in the decomposition of iodide of

\* Hydrogen lost.

amyl are identical; and hence we may assume generally that the action of zinc upon an alcohol-iodide ( $C_n H_{(n+1)} I$ ) and the electrolysis of an acid  $C_{(n+2)} H_{(n+2)} O_4$ , give rise to the formation of the same compound.

The products collected above and below amyl, contain other products besides amyl; but we are not at present in possession of sufficient data to form a correct idea respecting the nature of these substances. From the analogous observations of Dr. Kolbe in the valeric series, we should expect to meet in the lower fraction, the hydrocarbon  $C_{10} H_{10}$  and fusel-oil, arising from the decomposition of the compound ether,  $C_{10} H_{11} \cdot C_{12} H_{11} O_4$ , by the contact of the crude oil with potassa. We have not as yet studied this question with sufficient accuracy; but it may be even now stated that, in the lower fraction, we have not, up to the present moment, been able to detect fusel-oil. Moreover the existence of an ether  $C_{10} H_{11} \cdot C_{12} H_{11} O_4$ , in the crude product of the electrolysis, is not supported by the results of observation: for this compound ether, which would be nothing else than the caproate of amyl, prepared by us as stated above, boils at  $211^\circ C.$  ( $411^\circ 8 F.$ ), whilst the crude product entirely distilled below  $180^\circ C.$  ( $356^\circ F.$ ) However, we leave this question open, and are satisfied to have established by experiment, the analogy of the principal metamorphosis of valeric and caproic acids, under the influence of the galvanic current.

#### DECOMPOSITION OF CENANTHYLIC ACID UNDER THE INFLUENCE OF THE GALVANIC CURRENT.

Incidentally to the experiment with caproic acid, we have also subjected cenanthylic acid to the action of the pile.

The acid which served us for the experiments communicated in the remaining portion of our paper, was prepared in the manner recommended by Tilley,\* by acting upon the oil of *Ricinus communis* with dilute nitric acid. By this means, with considerable patience, a sufficient amount was obtained. We have tried various other processes, oxidation of the oil with chromic acid or a mixture of bichromate of potassa with sulphuric acid, or treatment of cenanthale with various oxidizing agents; but we have invariably found that the action of nitric acid on the oil, although tedious in the extreme, still gives the best results. The crude acid was repeatedly washed, and afterwards redistilled with water, in order to ensure its perfect purity. As it is partially decomposed by distillation alone,

\* Chem. Soc. Mem. I.

we tested its purity by the analysis of a silver-salt in preference to taking the boiling-point.

0.2324 grms. of silver-salt gave :

0.1052 „ „ silver,

yielding a percentage of 45.30 of silver.

Theory requires 45.56 of silver.

The potassa-salt was easily made by neutralizing the acid with pure carbonate of potassa. This salt is not crystallizable; it is easily soluble in water.

The phenomena, observed in the decomposition of cenanthylic acid, are perfectly analogous to those exhibited in the electrolysis of caproic and valeric acid,—evolution of carbonic acid and hydrogen, separation of an oily layer in the decomposing apparatus, and formation of carbonate and bicarbonate of potassa in the residuary aqueous solution.

The oily layer, which had an ethereal odour and a sweetish taste, was separated, dried, and subjected to distillation. It boiled between 130° (266° F.) and 230° (446° F.), the thermometer exhibiting a tendency to become stationary towards 190° (374° F.) Near the close of the operation, the liquid assumed a dark-brown colour, and a considerable quantity of charcoal remained in the retort. The separation of the various constituents of the oil was effected by treatment with an alcoholic solution of potassa, exactly as in the product obtained from caproic acid.

However, as we performed these experiments upon a somewhat larger scale, we took care to establish by analysis the nature of the acid remaining in form of a potassa-salt. For this purpose, the acid was separated by hydrochloric acid, washed, converted into the ammonia-salt, and subsequently into the silver-salt.

0.4965 grms. of silver-salt gave :

0.2260 „ „ silver = 45.51 per cent.

Theory requires 45.56 per cent.

These numbers establish, beyond doubt, the separation of cenanthylic acid by potassa, from the crude-oil product.

The alcoholic distillate, when treated with water, yielded an oily liquid, which, after being dried with chloride of calcium, boiled between 170° (338° F.) and 210° (410° F.); by far the largest quantity, however, distilled at 202° (395.6° F.) In fact, the thermometer became stationary at this temperature, even in the first rectification. The fraction collected round this point, when distilled, once more exhi-

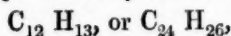
bited a perfectly constant boiling-point at  $202^{\circ}$  ( $395.6^{\circ}$  F.) This liquid had a very agreeable aromatic odour: it was insoluble in water, but miscible in all proportions with alcohol and ether. Analysis gave the following results:

I.	0.2245	grms. of substance gave,
	0.6940	„ „ carbonic acid, and
	0.3160	„ „ water.
II.	0.3345	„ „ substance gave,
	1.0370	„ „ carbonic acid, and
	0.4650	„ „ water.

Percentage-composition:

	I.	II.
Carbon . . .	84.49	84.54
Hydrogen . . .	15.60	15.44

These numbers correspond closely with the formulæ,



as may be seen from the following comparison:

	Theory.		Mean of experiment.
12 eqs. of Carbon . .	72	84.70	84.52
13 „ „ Hydrogen . .	13	15.30	15.52
1 „ „ Caproyl . .	85	100.00	

The formula  $C_{12}H_{13}$ , homologous to those of methyl, ethyl, &c., would represent the radical of an alcohol,  $C_{12}H_{14}O_2$ , standing to caproic acid in the same relation as acetic acid stands to wine-alcohol. This alcohol might be termed caproylic alcohol, and the corresponding radical hydrocarbon, caproyl. The nomenclature of this series is so sadly embarrassed by the accumulation of similar names in the eighth and tenth family, that—objectionable though the rechristening of chemical compounds may be—we believe that the suggestion of more appropriate names for caprylic and capric acids, would meet the general approbation of chemists.

It would have given us much pleasure to have studied the deportment of caproyl under the influence of re-agents, the more so, as the pinions of chemists are divided respecting the formulæ of the so-called radicals, some of them adopting expressions corresponding to 2 volumes of vapour, others preferring 4 volumes in a formulæ. The study of the products of decomposition of caproyl might have decided this question; but unfortunately the limited quantity of substance at our disposal

prevented us from following out this direction of the enquiry. Moreover, caproyl exhibits but little disposition to furnish readily accessible products.\*

We mention only that the substance is not affected by concentrated sulphuric acid, and that it may be distilled with moderately concentrated nitric acid, without undergoing any change. It was only by distillation with a mixture of the two acids, that a very slow, and even then incomplete oxidation took place. After repeated distillation, the distillate was mixed with water; the supernatant oil, separated by a pipette, and heated with ammonia, dissolved but partially. The ammoniacal solution contained an oily acid, which separated on addition of a mineral acid, and exhibited the odour of caproic acid. We converted the remaining solution, after boiling off the excess of ammonia, into a silver-salt, which was deposited as a whitish, very difficultly soluble powder. After recrystallization, it was obtained in slightly yellow crystals, which gave on analysis the following results:

I. 0.2145 grm. of silver-salt gave:  
0.1055 „ „ silver.

A second specimen, prepared in a similar manner, was analysed in the same way; during ignition a slight deflagration took place.

II. 0.1486 grm. of silver-salt gave:  
0.0686 „ „ silver.

Percentage:

	I.	II.
Silver . . .	49.13	46.16

The theoretical percentage of silver in the caproate is 48.65, and in the nitrocaproate 40.30; the first analysis exhibits a slight excess, which may be due to reduction of a small quantity of silver during the recrystallization of this rather difficultly soluble salt. The deficiency of the second may possibly be owing to the presence of a

\* The remarkable unalterability of the so-called radicals, when contrasted with the want of stability of the higher homologues of marsh-gas—as indicated by the non-production of these substances in the reaction of alkaline earths upon the higher terms of the series  $C_n H_n O_4$ —appear to discountenance more and more the assumptions of the identity of the two classes of compounds. As I had an opportunity of suggesting at an earlier period (Chem. Soc. Qu. J. III, 133), the radicals may be only isomeric with the marsh-gas series. This, of course, does not interfere in the slightest degree with the adoption of 4 volume formulæ; nor does the conversion of caproyl into caproic acid, which I consider established by the experiments of Messrs. Brazier and Gossleth, in my opinion, militate in the slightest degree against the admission of the higher formulæ.—A. W. H.

small quantity of nitrocaproic acid, a supposition which is supported by the slight deflagration during combustion, and by an analogous observation of Dr. Kolbe,\* in the oxidation of butyl. We are sorry that our results are not more definite, but hope their insufficiency will be excused by the difficulty attending these operations. We have no doubt in our own minds that the acid produced under these circumstances is caproic acid.

Bromine has scarcely any action upon caproyl, not even under solar irradiation.

Chlorine acts very powerfully even in diffused day-light, torrents of hydrochloric acid being immediately disengaged. The caproyl is rapidly converted into a viscous mass, which, being decomposed on ebullition, with evolution of hydrochloric acid and deposition of carbon, could not be purified for analysis. Even by a very moderate action of chlorine, we did not succeed in obtaining a direct compound of caproyl with chlorine.

In conclusion, we have to add that we have made a few experiments with the oil which passed over before caproyl, in the rectification of the liquid separated from the alcoholic distillate after treatment with potassa. This substance, which has an aromatic odour and sweet taste, was several times redistilled, when a compound was obtained boiling pretty constantly at  $175^{\circ}$  ( $347^{\circ}$  F.) Analysis with protoxide of copper gave the following results:

0.3220 grm. of substance gave :  
 1.0070 " " carbonic acid, and  
 0.4225 " " water.

Percentage-composition.		Theoretical values of $C_n H_n$ .	
Carbon . . .	85.29	Carbon . . .	85.72
Hydrogen . .	14.57	Hydrogen . .	14.28

These numbers show that the liquid in question is a hydrocarbon of the family  $C_n H_n$ , the slight deficiency in the carbon and the excess in the hydrogen, being evidently due to the presence of a trifling quantity of caproyl.

We have no direct data for the value of  $n$ ; the boiling-temperature would point to the formula  $C_{24} H_{24}$ .

We have not met among the products obtained in the electrolysis of cœnanthyllic acid, with the hydrocarbon caproylene, (oleylene)  $C_{12} H_{12}$ , or with caproylic alcohol, the formation of which substance we might have expected from the analogous department of valeric

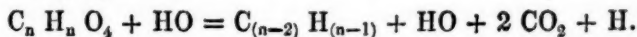
\* Chem. Soc. Qu. J. II, 163.



acid; we cannot, however, adduce any positive evidence as to the absence of small quantities of these substances. The question, what compound in the crude oil gives rise to the formation of the cœnanthylic acid, whether it be a kind of compound ether or an aldehyde, &c. has still to be answered by further experiments.

One point, however, appears to be fixed by the preceding experiments, namely, that the members of the series  $C_n H_n O_4$ , when treated with the galvanic current, invariably give rise to the formation of a hydrocarbon closely connected with the series following one step lower on the scale of organic compounds, hydrogen and carbonic acid being simultaneously eliminated.

Generally expressed, this metamorphosis would be represented by the following equation:



This equation shows that formic acid, when exposed to the current, can yield only hydrogen and carbonic acid. Together with this principal metamorphosis, several secondary changes appear also to occur, whose nature, however, is not yet perfectly understood. It deserves moreover to be noticed, that these latter changes, far from presenting the constant character of the chief decomposition, appear to vary with the position of the substances examined upon the ladder of combustion.

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#### XXIV.—*Creatine a constituent of the Flesh of the Cetacea.*

By DAVID S. PRICE, Ph. D.

A fine specimen of the Rorqual Whale (*Balenoptera musculus*), having been brought into Margate in February last, I availed myself of the opportunity afforded of ascertaining whether creatine, which has been found to be a constituent of the muscles of various mammals, birds, and fishes, was likewise contained in those of the cetacea. It has been shown by Liebig that the muscles of fat animals yield a much smaller quantity of this substance than those of lean ones; and as the whale may be ranked pre-eminently among the former, it was deemed necessary, in order to ensure a decided result, that a large quantity of the flesh should be employed. For this purpose about 40 lbs., the freest from fat that could be selected, were treated in the manner described by Liebig in his research into the constituents of the juices of the flesh; 10 lbs. of the flesh were cut into small pieces, and well kneaded with an equal weight of cold water. The

flesh was then removed to another vessel holding the same amount of water, and after being again well pressed, was put in linen bags into a strong screw-press, and as much of the liquor obtained as possible; the second water served as the first receptacle for another 10 lbs. of flesh, which were treated in like manner, &c. In this way the extract from the 40 lbs. was eventually obtained. The large quantity of fat which collected on the surface of the fluid had to be removed prior to the liquid being strained through flannel bags for the purpose of separating any muscular fibre and fatty matter that might be suspended in it. The filtered liquid, which was of a blood colour and exhibited an acid reaction, was heated in large evaporating pans over a water bath, whereby the albumen was coagulated, taking with it nearly the whole of the colouring matter, the liquid, on being strained through linen bags, retaining only a very faint colour.

The odour and flavour of this filtrate was not distinguishable from that of the extract of beef. In order to separate the last traces of albumen, the liquid extract was rapidly heated to ebullition over a strong fire in a tinned copper vessel. After being filtered, the solution was mixed with concentrated baryta-water till a precipitate ceased to be formed, a point which was reached long after the acid reaction had disappeared. The almost colourless filtrate, when evaporated in the water bath, acquired a dark brown colour, and became gradually gelatinous, emitting an odour very similar to that of glue. The concentrated liquor was now placed in a cool situation in several shallow vessels, when, after the lapse of forty-eight hours, numerous minute glittering crystals were deposited, which, owing to their great specific gravity, could be easily separated by decantation of the supernatant liquid. When dried in this minute state, these crystals presented a beautiful appearance, refracting light with remarkable intensity. After three or four crystallizations, they may be obtained quite pure. If their aqueous solution be allowed to crystallize slowly, crystals one quarter of an inch in length are formed, presenting a silky lustre, and frequently arranged in groups. These crystals are insoluble in alcohol, but very soluble in boiling water; when warmed on platinum foil, they lose their lustre, becoming opaque and white; when heated more strongly, they carbonize, emitting the odour of burning nitrogenous substances; on the application of a still stronger heat, the carbon is entirely consumed, no ash remaining behind.

0.3097 grms. of this substance, when kept for some time in a water bath at a temperature of  $212^{\circ}$  F., lost 0.0378 grms.,

corresponding to 12.2 per cent of water, the amount found by Liebig in creatine prepared from different sources.

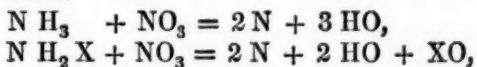
I must not forget to state that I obtained this substance (a specimen of which I have the honour to lay before the Society) in very small quantity. There can be no doubt as to the identity of this body with that described by Chevreul, Liebig, Schlossberger and Gregory; and we may safely conclude that it is a constituent, in greater or less amount, of the fluids of the flesh of all the higher class of animals.

## XXV.—*Researches on the Volatile Organic Bases.*

BY DR. A. W. HOFMANN.

### VIII. ON THE BEHAVIOUR OF ANILINE AND THE ALCOHOL-BASES WITH NITROUS ACID.\*

Chemists are acquainted with the happy idea which led Piria† to examine the deportment of substances derived from ammonia under the influence of nitrous acid. The property possessed by nitrous acid of being reduced by ammonia with evolution of nitrogen, appeared likely to afford a simple method of effecting a regular oxidation of the derivatives of ammonia, or, in other words, of reconverting an amide into an oxide.



Piria has proved by experiment that oxamide, succinamide and butyramide, when treated with nitrous acid, are readily reconverted into the corresponding acids, nitrogen being evolved. He succeeded, moreover, by the aid of this process, in establishing the true character of two substances, asparagine and aspartic acid, which have henceforth to be considered as malamide and malamic acid.

At a later period, the same reaction was applied to several nitrogenous compounds of uncertain constitution, by M. Strecker.‡ This chemist found that hippuric acid, glycocine, and leucine, when treated with nitrous acid, exhibit a perfectly analogous deportment, the former yielding an acid  $\text{C}_{18} \text{H}_8 \text{O}_8$ , the two latter, terms of a very remarkable series of acids  $\text{C}_n \text{H}_n \text{O}_6$ , parallel, as it would appear, with the series of fatty acids.

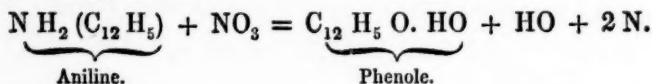
\* The former papers belonging to this series have been published. Chem. Soc. Qu. J. I, 159, 269, 285; II, 36, 300.

† Ann. Chim. Phys. [3] XXII, 160.

‡ Ann. Ch. Pharm. LXVIII, 55.

Among the various classes of nitrogenous substances, there is perhaps none which is likely to derive more benefit from this reaction than the group of organic bases. Connected as these substances are with ammonia by ties of greater or less intimacy, the observation of their deportment under the influence of this agent, opens a field of investigation, which up to the present moment has scarcely been entered upon.

The only base hitherto investigated in this direction, is aniline. Some experiments on the behaviour of this alkaloid have been communicated by Mr. T. S. HUNT,\* who found that this substance, when exposed to the action of nitrous acid, is converted into phenole, nitrogen being evolved.



This decomposition is quite in accordance, both with the results obtained in the metamorphosis of other substances by Piria and Strecker, and with the close relation existing between aniline and phenole—a relation which has been remarkably illustrated by the study of the derivatives of the two substances. Aniline, when treated with nitric acid, yields trinitrophenole, whilst chlorine gives rise to the formation of trichlorophenole; both aniline and phenole, when subjected to the action of chlorate of potassa and hydrochloric acid, are converted into chlorokinone (chloranile). Experiment, moreover, has shown that phenole may actually be converted into aniline, by exposure to the influence of ammonia at high temperatures.

The position, therefore, of aniline, as a member of the phenyl-group, scarcely required the additional support of its reconversion into phenole. Still, experimentally, this conversion offers considerable interest, inasmuch as it shows that this simple process admits of eliminating the nitrogen from compounds which are capable of resisting the most powerful agents at our disposal. It is well known that the vapour of aniline may be passed over ignited soda-lime without undergoing decomposition, and that we are, consequently, obliged to introduce certain modifications† into the ordinary process for the determination of nitrogen.

The interest of the subject and, moreover, the fact of Mr. Hunt's investigation being entirely qualitative, induced me to repeat his experiment, with the view of proving the relation existing between aniline and phenole by definite numbers.

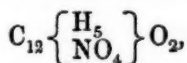
\* Sill. Am. S. Nov. 1849.

\* Chem. Soc. Qu. J. I, 159.

Mr. Hunt has performed the experiment in two different ways, namely: 1. By exposing a mixture of the base with nitric acid of a given strength to the action of binoxide of nitrogen, as originally proposed by Piria.—2. By acting upon hydrochlorate of aniline with solution of nitrite of silver. He obtained by both methods a dark-brown oil, soluble in potassa, possessing the odour of castoreum, and an acrid taste, and yielding with nitric acid, nitrophenisic acid (trinitrophenole).

By following the former of the two processes, adopting exactly the circumstances and proportions indicated, I never succeeded in obtaining a substance from aniline which I could with certainty have declared to be phenole. Invariably a dark-brown resinous mass was formed, which indeed had the odour of castoreum, and was soluble in a great excess of potassa, but from which no phenole in a state of purity could be obtained.

Nor was the experiment attended with better results when the circumstances were slightly modified by substituting a weaker or a stronger acid. I found that either no action at all took place, or the metamorphosis went too far, the aniline being converted into the brownish resinous mass. This mass may contain traces of phenole, but it consists chiefly of a brown uncrystallizable substance, together with a crystalline compound of most remarkable beauty, which I subsequently obtained in larger quantity, when acting upon aniline with a mixture of nitric and arsenious acid, from which I had anticipated a result analogous to that obtained by Mr. Millon, in the preparation of chlorous acid. This substance is nitrophenole,



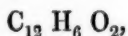
which may be likewise obtained by acting with dilute nitric acid upon phenole itself. The study of this compound, which furnishes several links of connection between the phenole-family and various other groups, will be the subject of another communication to the Society.

The presence of free nitric acid interfering sadly with the conversion of aniline into normal phenole, yielding as it does, according to the concentration of the acid, products derived from this compound by a more or less advanced substitution; I availed myself of the second process, namely: decomposition of the hydrochlorate of aniline with nitrite of silver. This experiment yielded a totally different result. As soon as the two substances come into contact, torrents of pure nitrogen gas are evolved, the whole liquid becomes turbid from the

separation of oily globules which are likewise of a very dark colour, from which, however, pure phenole may be prepared without much difficulty. When separated from the liquid by means of ether, and subjected, after the removal of the ether by evaporation, to distillation with water, they yield a quantity of a perfectly colourless oil; but even in this process a considerable portion of resinous substances is produced. The oil separated from the water and rectified over anhydrous phosphoric acid, passed over in the form of a limpid liquid which solidified after a short time into a mass of white crystals, possessing all the properties of phenole. Analysis with protoxide of copper gave the following results:

0.3080 grms. of crystal gave :  
 0.8605 " " carbonic acid, and  
 0.1780 " " water.

These numbers lead to the percentage which I subjoin to the values required by the formula



	Theory.		Experiment.
12 equivs. of Carbon . .	72	76.50	76.22
6 " " Hydrogen . .	6	6.38	6.38
2 " " Oxygen . .	16	17.02	—
1 " " Phenole . .	94	100.00	

These numbers leave no doubt respecting the transformation of aniline into phenole by the action of nitrous acid.

The method of employing the nitrous acid in form of a silver-salt, or, as I have invariably done in subsequent experiments, in the form of a potassa-salt,\* eliminates in a happy manner the difficulties attending the use of so powerful an agent as nitric acid, under whose influence a great many substances would undergo further transformations.

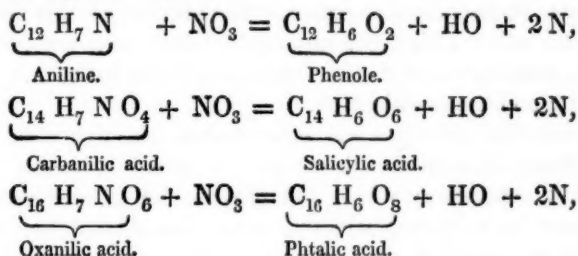
The conversion of aniline into phenole by this method, renders it probable that the derivatives of aniline, the anilides, will admit of similar transformations. The action of nitrous acid would thus afford a general passage from the anilides to the phenides.

Carbanilic acid would in this manner yield salicylic acid (carbophenylic acid), oxanilic acid might be converted into phtalic acid (oxaphenylic acid), relations of these acids with the aniline-series

\* The crude nitrite containing free potassa, together with undecomposed nitrate as obtained by decomposing nitre, may be employed with perfect success.



being undeniable, the former passing into aniline through phenole, the latter through benzole.



Whether the anilides are actually affected by nitrous acid, and whether, if such be the case, the products formed are identical or isomeric with the substances which theory appears to suggest, has to be decided by further experiments.

The facility with which aniline is converted into phenole, standing to it in the position of an alcohol, induced me to perform some corresponding experiments with the bases of the series  $\text{C}_n \text{H}_{(n+3)} \text{N}$ . This series attracted my attention particularly, since it is at present much more complete than the series of collateral alcohols  $\text{C}_n \text{H}_{(n+2)} \text{O}_2$  as seen from the following conspectus.

Methylic alcohol . .	$\text{C}_2 \text{H}_4 \text{O}_2$	Methylamine . .	$\text{C}_2 \text{H}_5 \text{N}$ .
Ethylic alcohol . .	$\text{C}_4 \text{H}_6 \text{O}_2$	Ethylamine . .	$\text{C}_4 \text{H}_7 \text{N}$ .
Propylic alcohol . .	?	Propylamine . .	$\text{C}_6 \text{H}_9 \text{N}$ .
Butylic alcohol . .	?	Butylamine . .	$\text{C}_8 \text{H}_{11} \text{N}$ .
Amylic alcohol . .	$\text{C}_{10} \text{H}_{12} \text{O}_2$	Amylamine . .	$\text{C}_{10} \text{H}_{13} \text{N}$ .

Whilst methylamine, ethylamine, and amylamine, have been formed with the assistance of the alcohols themselves, propylamine (onylamine, metacetamine) and butylamine (petinine) have been derived from sources perfectly unconnected with alcohols, the former being produced, according to Wertheim,\* from narcotine, by the action of alkalies, whilst the latter was found by Anderson† amongst the products of distillation of animal substances. A deportment of this series with nitrous acid, analogous to that exhibited by aniline, would have put us in the possession of the missing alcohols.

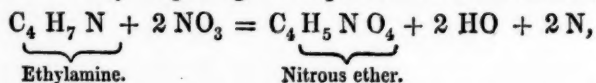
The change which these substances undergo is not perfectly similar to that of aniline. The first experiments which I performed, were made with ethylamine. On distilling a mixture of hydrochlorate of ethylamine with either nitrite of silver or nitrite of potassa, a violent effervescence of nitrogen took place, and an aqueous liquid

\* Ann. Ch. Pharm. LXXIII, 208.

† Phil. Mag. [3] XXXIII, 174.

passed over which contained no alcohol or mere traces of it, whilst a yellowish oil, of a penetrating aromatic odour and a sweet but pungent taste, floated on the surface. The amount of this oily liquid—which had rather a high boiling-point—being quite out of proportion with the quantity of ethylamine employed, I was led to subject the gas evolved to a closer examination.

I found that this gas was inflammable, burning with the green-edged flame of nitrous ether, that it dissolved partly in water, yielding a solution in which the presence of nitrous acid could be ascertained by sulphuric acid and green vitriol, and from which the gas could be expelled again by heat. The experiment being performed during hot weather, I endeavoured to condense the ether by passing the disengaged gas through a glass serpentine placed in a frigorific mixture. I did not succeed, however, in collecting the liquid ether. This compound is diffused in so bulky a volume of nitrogen, that its condensation would require both the employment of a larger quantity of ethylamine than I had at my disposal, and the use of more efficient refrigeration, and perhaps even preliminary absorption of the ether-compound in alcohol. However, be this as it may, the action of nitrous acid upon ethylamine gives rise to the formation of a considerable quantity of nitrous ether, other substances being formed at the same time. The conversion of ethylamine into nitrite of ethyl requiring two equivalents of nitrous acid,



it appeared that the production of the latter might be greatly facilitated by the action of the nitrite upon an acid solution of the base. Experiment has borne out this anticipation. In fact, it suffices to throw into a solution of hydrochlorate of ethylamine, mixed with its own bulk of hydrochloric acid, a crystal of nitrite of potassa, when at once, together with nitrogen, nitrous ether is evolved in considerable quantity, the vapour of which may be lighted at the mouth of the test-tube. In this manner, the conversion can be readily exhibited in a lecture-experiment.

The yellow aromatic oil which is formed, together with the nitrous ether, and the production of which, I must add, is not prevented by the use of an acid solution, is obtained in so limited a quantity, that I have not yet been able to subject it to a closer examination, attractive though the study of a substance produced under so peculiar circumstances must be.

I would not have dared to affirm, on the ground of the experiments

detailed, the generation of nitrous ether in the above reaction, had I not acquired additional support for this position by repeating the same experiment in a less volatile series, occupying a higher position in the system.

In their researches on caproic acid, Messrs. Brazier and Gossleth had obtained a considerable quantity of amylamine, as a secondary product, which these gentlemen kindly placed at my disposal for the experiment. Hydrochlorate of amylamine, when submitted to the action of a nitrite, exhibits exactly the same deportment as ethylamine. The experiment is best performed by heating a solution of nitrite of potassa in a flask connected with a condenser, and adding the solution of hydrochlorate of amylamine acidified with hydrochloric acid, in small portions through a funnel-tube, the violent effervescence produced upon each addition being allowed to subside before pouring in a new quantity. By this means, an aqueous distillate is obtained, with a yellowish oily layer floating upon its surface, exhibiting in a remarkable manner the peculiar odour of nitrite of amyl, which for the sake of comparison had been prepared from fusel-oil. The oily substance being separated by means of a pipette, the aqueous liquid yielded a little more by saturation with common salt. The whole quantity of oil obtained in this manner amounted to about  $\frac{1}{8}$ th of an ounce. When dried and subjected to distillation, the thermometer showed that it was a mixture, ebullition commencing at about  $90^{\circ}$ , the thermometer rising slowly to about  $110^{\circ}$ , and then gradually to  $200^{\circ}$ , a small quantity of carbon remaining in the retort. During the first part of the distillation, a perceptible evolution of red vapours took place, evidently arising from the partial decomposition of the nitrite of amyl. A comparative experiment with nitrite of amyl, prepared from fusel-oil, yielded the same result. The fraction collected between  $90^{\circ}$  and  $110^{\circ}$ , when redistilled, exhibited a tendency towards a constant boiling-point a little below  $100^{\circ}$ . The thermometer, however, rose to nearly  $170^{\circ}$  towards the close of the operation, showing that the nitrite of amyl still contained a considerable quantity of other substances. Lest too much should be lost by further rectification, the portion collected just below  $100^{\circ}$  was subjected to combustion.

0.3110 of oil gave :

0.6125 „ carbonic acid, and

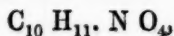
0.2900 „ water.

Percentage

Carbon . . . . . 53.7 ;

Hydrogen . . . . . 10.36

The formula



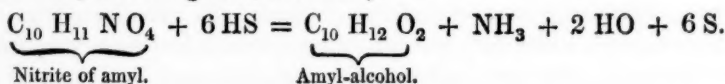
requires

Carbon . . . . . 51.21

Hydrogen . . . . . 9.41

These numbers showed that the nitrite under examination was still mixed with a quantity of a substance containing more carbon and hydrogen. The boiling-point of pure nitrite of amyl, according to Balard's experiment, is  $96^{\circ}$ .

Not satisfied with these approximate numbers, I endeavoured to obtain additional evidence by the conversion of the nitrite into fusel-oil. After having established, by experiment, that nitrite of amyl, like its homologue in the ethyl-series, when treated with hydrosulphate of sulphide of potassium, gives rise to the formation of the correlative alcohol, with formation of an alkaline polysulphide and ammonia, according to the formula,



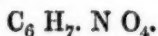
I subjected the impure nitrite to the same treatment. A violent reaction took place, in which the separation of ammonia and sulphur could be traced without difficulty. The resulting fusel-oil, at once evident by its nauseous odour, was, moreover, converted into sulphamylic acid, by dissolving it in sulphuric acid (when a small quantity of the aromatic oil remained uncombined), and subsequently transformed into a baryta-salt.

These experiments leave no doubt respecting the formation of nitrite of amyl by the action of nitrous acid upon amylamine. In the same reaction, however, other substances are formed; I say substances, because the aromatic oil which boils at the higher temperature, when allowed to stand, gradually deposits a quantity of shining crystals having a greasy appearance. The same substance, which is extremely fusible, is usually found to separate on the addition of water to the residue of chloride of potassium in the decomposing flask. I have, up to the present moment, not the slightest notion respecting the nature of these compounds.

Although the difficulty of perfecting these reactions appears at present altogether to preclude the possibility of arriving at the practical formation of propylic and butylic alcohols, I was, nevertheless, desirous to see whether propylamine and butylamine, would exhibit a similar deportment with nitrites.

For this purpose, I prepared a quantity of propylamine, according

to the directions given by Wertheim, by distilling narcotine with an excess of hydrate of potassa.\* The aqueous solution of propylamine, when supersaturated with hydrochloric acid, and treated with nitrate of potassa, gave rise to a powerful evolution of nitrogen, accompanied by an inflammable gas, burning with a green-edged flame. Accordingly, propylamine exhibits with nitrous acid a deportment similar to that of ethylamine; and from analogy, we may infer that the burning substance was the nitrous ether of propylic alcohol or nitrite of propyl,



I am indebted to the kindness of Dr. Anderson of Edinburgh, for a small quantity of butylamine prepared by him from Dippel's oil. When dissolved in hydrochloric acid, and treated with the nitrite, this base likewise evolved a considerable quantity of nitrogen, but no inflammable vapour. The latter circumstance is readily intelligible, if we recollect that nitrite of butyl would boil at a rather high temperature, at about  $80^\circ$ , a temperature high enough to prevent the compound from evaporating in sufficient quantity in the gas evolved. When the operation was performed in a small retort, the evolution of nitrogen was attended with the separation of small oily globules, which floated upon the water, running down the condenser; but were dissolved again before reaching the receiver, in which an aqueous liquid of a very peculiar odour was collected. Analogy allows us to infer, that in this reaction, nitrate of butyl,  $\text{C}_8 \text{H}_9 \text{N O}_4$ , the nitrous ether of the butyl-series, is formed.

The regeneration of the alcohols from the nitrites by means of hydrosulphuric acid, having been established by experiment, it is evident that the deportment of propylamine and butylamine with nitrous acid may one day become the key to the formation of their collateral alcohols, as soon as the progress of science shall have taught us simpler and more abundant sources of these bases.

In conclusion, I wish to draw the attention of the Society to the light which the preceding experiments appear to throw upon some earlier investigations.

In 1845, M. Gerhardt observed that the action of nitric acid upon brucine gives rise to the evolution of a gas which burns with a green flame, and exhibits some of the properties of nitrous ether. The formation of this ether in the process alluded to, was subsequently

\* By the distillation of narcotine with potassa, in addition to an aqueous solution of propylamine, an oily base, boiling apparently at a very high temperature, was formed, which deserves to be examined. The odour of propylamine remarkably resembles that of lobster in an early stage of putrefaction.

doubted by Liebig, who, on repeating the experiment, obtained a liquid boiling at a temperature (from  $70^{\circ}$  to  $75^{\circ}$ ), much higher than the boiling-point of nitrous ether ( $16^{\circ}5$ ). It is evident that the action of nitric acid upon brucine induces the formation of various substances. The existence among the natural alkaloids of ethylated bases, which I suggested on a former occasion, and which appears to be borne out by new facts, such as the formation of methylamine from caffeine or of propylamine from narcotine, renders it probable that part of the metamorphosis caused by nitric acid, is due to the formation of nitrous acid, which subsequently acts as in the foregoing experiments. I have distilled an acid solution of hydrochlorate of brucine with nitrite of potassa, and find that this reaction gives rise to the evolution of a considerable quantity of the inflammable gas burning with a green-edged flame, which is obtained by directly dissolving brucine in nitric acid.

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#### XXVI.—*Researches on Pelargonic Acid.*

BY M. AUGUSTE CAHOURS.

(LETTER TO DR. A. W. HOFMANN.)

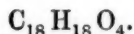
The action of nitric acid on the essential oil of rue gives rise to several homologous acids. The first term of this series, to which I have given the name *Rutic acid*, only differs from the oil itself by containing two equivalents of oxygen more: the latter stands, therefore, to the former in the relation of an aldehyde. The action of nitric acid, however, is not confined to a simple oxidation of the essential oil; according to the duration of the action,  $(C_2 H_2)$ ,  $2 (C_2 H_2)$ ,  $3 (C_2 H_2)$ , are successively oxidized,—pelargonic, caprylic, and cœnanthylic acids, and probably other more simple terms of the same series being formed. It is evident that, in employing commercial acid, and allowing it to act for some time on the oil, several of these products are finally obtained, the one predominating over the others according to the duration of the reaction.

Pelargonic acid being the one least known of this group, and being also obtained the most plentifully from oil of rue, I turned my attention to it in preference; its study has furnished me with the following results:

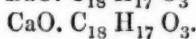
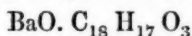
Pure pelargonic acid is colourless, assuming an amber tint after a time. It boils steadily at  $260^{\circ}$ , and distils without undergoing alteration or change of colour, if the precaution be taken to perform



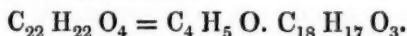
the distillation in an atmosphere of carbonic acid. The analysis of several specimens has furnished me with numbers leading to the formula,



This acid forms soluble and crystallizable salts with potassa, soda and ammonia. With baryta and strontia it yields salts slightly soluble in water and soluble in boiling alcohol, from which solution they separate on cooling in the form of crystalline scales of nacreous appearance. The analysis of these salts led to the formulæ,



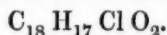
If a current of hydrochloric acid gas be passed into an alcoholic solution of pelargonic acid, an amber-coloured oil soon separates and floats on the surface; this oil, treated with a solution of carbonate of soda, washed with pure water, dried over chloride of calcium, and distilled, is obtained as a colourless liquid, the density of which is 0.86; its boiling-point is between 216° and 218°. The analysis of this product led to the formula,



On ebullition with a concentrated solution of caustic potassa, alcohol and pelargonic acid are reproduced.

Pentachloride of phosphorus acts very violently on pelargonic acid, hydrochloric acid gas being abundantly evolved; if the experiment be performed in a distilling apparatus, a colourless limpid distillate is obtained, which contains a large quantity of oxychloride of phosphorus; on re-distilling this product and rejecting the portion which passes over before the temperature becomes stationary, a limpid liquid is obtained as the latter portion of the distillate, which is heavier than water and boils at 220°. This liquid which gives off dense fumes when exposed to the air, and has a very powerful odour, evolves much heat when brought in contact with alcohol, pelargonic ether being formed.

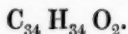
The analysis of this product led to the formula,



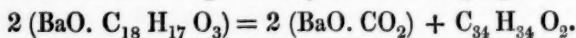
It is, therefore, the *Chloride of Pelargyl*.

Pelargonate of baryta is decomposed by dry distillation, a residue of carbonate of baryta being obtained, a brownish oil collecting in the receiver, which solidifies on cooling. This substance, when pressed between bibulous paper, yields a solid product easily soluble in ether. The ethereal solution, submitted to spontaneous

evaporation, deposits large crystalline plates, assuming a nacreous appearance on desiccation. This product, submitted to analysis, yielded numbers coinciding with the formula,



This substance is, therefore, *Pelargone*, isomeric with margaric aldehyde. Its formation is explained by the following equation:



Pelargone is violently attacked by fuming nitric acid, a nitrogenous acid being formed, which is doubtless a homologue of that obtained by the similar treatment of butyrone.

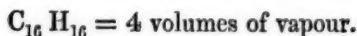
If we assume that the action of an excess of alkaline base, at a high temperature, on the acids of the acetic series, give rise to phenomena similar to those observed with benzoic acid or acetic acid itself, we should expect to obtain, by the distillation of pelargonic acid with an excess of potash-lime, either the valyl of Kolbe, or a compound isomeric with it; this presumption is not however, confirmed by experiment.

On submitting a mixture of pelargonic acid with from four to five times its weight of potash-lime to a temperature nearly approaching a dull red-heat, a large quantity of gas is disengaged, some volatile products are condensed and a residue of partially carbonated alkali is obtained. On passing the gas into bromine, a portion is absorbed, and the rest passes through unaltered. The portion absorbed by the bromine forms with this substance a very dense liquid, which, when treated with a very weak solution of potassa in order to remove the excess of bromine, yields an amber-coloured heavy liquid, consisting of three different substances; the one boils at  $130^\circ$ , and crystallizes when the vessel containing it is immersed into powdered ice, this is *Dibromo-mylenes*  $\text{C}_4 \text{H}_4 \text{Br}_2$ ; the second boils at  $143^\circ$  to  $144^\circ$ , and is the *Dibromo-propylene*  $\text{C}_6 \text{H}_6 \text{Br}_2$ ; the third, which boils at  $160^\circ$ , is *Dibromo-butylene*  $\text{C}_8 \text{H}_8 \text{Br}_2$ . The first and particularly the latter of these substances, are present in very small quantity compared to the propylene-compound.

The liquid product of this reaction is of a complex nature, the larger portion boils between  $105^\circ$  and  $110^\circ$ ; the latter portion distils at  $136^\circ$ .

Several analyses made with different specimens of the liquid, which boiled between  $106^\circ$  and  $110^\circ$ , have given me, as a mean, 84.9 of carbon and 14.8 of hydrogen, that is to say, more hydrogen and less carbon than in olefiant gas; the idea naturally suggested itself that this liquid might be a mixture of valyl and of a hydrocarbon of the series

$C_n H_n$ , having a very proximate boiling-point; some experiments, however, soon convinced me of the absence of valyl, this liquid being violently attacked by some reagents that have no action on valyl. The vapour-density of this substance was found to be 3.98, which leads to the formula,



This substance, therefore, would appear to be a hydrocarbon, homologous to olefiant gas, mixed with a small quantity of foreign matter. When treated with bromine it evolves heat, yielding a liquid having an aromatic odour. The analysis of this liquid yielded numbers leading to the formula,



The gas which is not acted on by bromine consists of hydrogen and another gas containing carbon, which is probably marsh-gas. The deportment of pelargonic acid accordingly differs in this instance essentially from that of its homologue, acetic acid; the carbon-hydrogen  $C_{16} H_{18}$ , which should be produced in this reaction, appears to be possessed of but little stability, splitting up, as it does, into hydrogen and marsh-gas.

It is probable that all the acids of the acetic series furnish analogous results. I have convinced myself that this is the case at least with caprylic and cœnanthylic acids.\* I am just now studying ethalic and margaric acids with the same view.

## XXVI.—On the Red Colouring Matters of Madder.

By ADOLPH STRECKER.

There is scarcely any class of bodies in organic chemistry, the investigation of which is attended with so many difficulties as that of the colouring matters; this may account for the imperfect knowledge we as yet possess of these substances, excepting indigo, which has been studied in every direction. Of many colouring matters we scarcely know more than the existence, while of others we possess the percentage-composition, translated into a more or less fitting empirical formula; a few only of these substances have become of late so far accessible to us, as to enable us to acquire a knowledge of them, corresponding to the present demands

\* The same results are obtained in the distillation of valeric acid. Comp. Chem. Soc. Q. J. III.

of the science. This circumstance may be owing in some measure to the difficulty experienced in obtaining these substances in quantity sufficient for more accurate investigations, as they generally occur distributed in small proportions only, over a large amount of other matter, besides which, on the other hand, the feebly defined and generally acid character of the colouring matters renders the preparation of definite compounds of them a matter of difficulty.

Madder ranks in importance before all other colouring principles; the cultivation of the *Rubia tinctoria*, the preparation of the madder, and, above all, its manifold applications in the dyeing of cotton and in calico-printing, in which it affords the most varied, beautiful, and durable colours, form important branches of agriculture and manufactures.

Since Kuhlmann\* first took up the chemical investigation of madder, many chemists have applied their talents and powers to this subject; and it must be gratefully acknowledged that the labours of Robiquet and Colin† Runge,‡ Schunck§ and Debus,|| have thrown much light on the chemical deportment of the active principles of the madder-root.

A superficial contemplation of the results of these researches would certainly appear to point out a great want of accordance between them; but on a more strict examination, the identity of the results may be discerned, and the differences in the statements easily explained and adjusted.

The study of the various researches on madder, together with comparative experiments made with this substance and with the splendid preparations of Messrs. Robiquet, Schunck and Debus, for the use of which I am indebted to Professor Liebig and Dr. Debus, have shown me that madder contains—besides the yellow or orange colouring matters, which do not play any important part in dyeing—two red colouring matters, which have been obtained by chemists in a state of greater or less purity, and have received from them various names.

The one of these, first prepared by Robiquet and Colin, and named by them *Alizarine*, was afterwards obtained in a state of perfect purity by Runge, who called it *Madder-red*. Persoz and

\* Ann. Ch. Phys. [2], XXIV, 225.

† Ann. Ch. Phys. [2], XXXIV, 225; LXIII, 306.

‡ J. Pr.Chem. V, 362.

§ Ann. Ch. Pharm. LXVI, 174.

|| Ann. Ch. Pharm. LXVI, 351.

Gaultier de Claubry,\* obtained it in a state of less purity, and described it under the name of *Matière colorante rouge*; and finally it was prepared perfectly pure by Schunck and Debus, and called, by the latter, *Lizaric acid*.

The second red colouring matter was first distinguished by Robiquet and Colin, by the name of *Purpurine*, although they did not obtain it pure; it was first isolated by Runge and called by him *Madder-purple*. Debus afterwards described it as *Oxylizaric acid*, and lately Higgin† obtained it mixed with alizarine, and described it under the latter name. Schunck has overlooked this substance; the correspondence of his analytical results with those of Debus, and some comparative experiments that I have instituted with the preparations of Schunck, Debus and Robiquet, show, however, that the alizarin of the first-named chemist is free from purpurine; and it is very probable that, in the treatment with concentrated solution of carbonate of potassa, the purpurine was dissolved, and only separated again in a decomposed form (possibly as alpha- or beta-resin).

#### ALIZARINE.

Alizarine is possessed of the following properties: it may be obtained in two forms, differing from each other in the amount of water which they contain. Hydrated alizarine occurs in small scales, having the appearance of mosaic gold. The anhydrous substance has a red colour, passing more or less into yellow, according to the thickness of the crystals. This explains the difference in the statements of Debus, Runge and Robiquet, who describe it, successively, as occurring in aurora-red needles, as a brownish-yellow powder, and of the colour chromate of lead. It fuses when heated, and sublimes in orange-coloured needles, a portion being decomposed with deposition of carbon, which may arise merely from the too rapid action of heat. It is moistened with difficulty by water, and, when boiled with the latter, dissolves with a deep yellow colour. The slightest trace of alkali (as ammonia or lime) colours the solution red; hence arises the fallacious statement of Robiquet that it dissolves in water with a rose-colour. It is considerably soluble in alcohol, to which it imparts a yellow colour, the solution becoming red under the same conditions as the aqueous solution. It dissolves likewise in ether with a yellow colour, which is not altered by the addition of small quantities of an

\* Ann. Ch. Phys. [2], XLVIII, 69.

† Phil. Mag. XXXIII, 282.

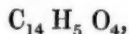
alkali, the resulting red alkaline compound being insoluble in ether. Alizarine is easily soluble in alkalis; its solution in hydrate of potassa or of soda appears, if sufficiently concentrated, of a deep purple colour by transmitted light and pure blue by reflected light; when highly diluted, the solution assumes a uniform violet colour. This readily explains why Robiquet and Runge state the solution to be violet-coloured, while Schunck calls it purple-coloured. Alizarine dissolves in ammonia and carbonate of ammonia with a colour similar to orchil, the solution possessing no blue appearance on the surface. The cause of the difference in colour of the solutions of alizarine in caustic or carbonated alkalis, evidently lies in the formation of different compounds of alizarine with the alkali. I prepared one of these in the following manner: Alizarine was dissolved, by the aid of heat, in a solution of carbonate of soda, saturated in the cold; the filtered solution deposited, on cooling, the compound of alizarine with soda, insoluble in concentrated soda-solution. This was dried, purified from an admixture of carbonate of soda by solution in absolute alcohol, and precipitated from this solution in purple flakes by addition of ether. It dissolved easily in water and alcohol with the colour of orchil; the solution was coloured blue by addition of caustic soda.

The compounds of alizarine with the alkalis are insoluble in cold concentrated salt solutions; the ammoniacal solution of alizarine gives with chloride of barium a nearly pure blue flocculent precipitate; the solution from which the precipitate has been separated by filtration is colourless. Acetate of lead gives a purple-red precipitate. A characteristic of alizarine is its insolubility in a cold solution of alum. When alizarine is boiled with a concentrated solution of alum, the liquid assumes a yellow colour, like that of an aqueous solution of alizarine; on cooling, the small quantity of alizarine that was dissolved separates again, the liquid becoming almost colourless. Alizarine forms a red solution in hydrated sulphuric acid, and is reprecipitated unchanged on the addition of water. Robiquet and Schunck have shown that alizarine is capable of producing, on mordantized cloth, all the colours obtained from madder. To conclude from this, that alizarine is the only active dyeing principle in madder, would certainly be going too far; for it will be presently shown that purpurine likewise yields durable and beautiful colours on mordantized cloths.

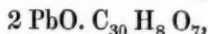
The results of the analysis of alizarine by Schunck and Debus, correspond exactly—nor does the older analysis by Robiquet differ considerably from their numbers. Schiel's results, however,



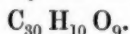
cannot be made to correspond with them. The percentage-composition of alizarine may perhaps be considered as established by the more recent analyses; but in the construction of its chemical formula, we meet with the difficulty of determining the equivalent of a weak acid by the preparation of neutral compounds. Schunck was led by the analysis of a lead-salt to the formula,



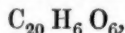
while Debus assigns to another lead-compound the formula,



and represents alizarine itself by the formula,



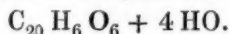
I believe I can prove that the chemical formula of alizarine is



which corresponds with sufficient accuracy with the percentage-composition of this substance and its compounds, and is likewise confirmed by the results of the decomposition of alizarine. The composition of alizarine, dried at  $100^\circ$  —  $120^\circ$ , is as follows:

Equiv.	Calc.	Schunck.			Found.	Debus.		
$\text{C}_{20}$	68.96	69.09	69.15	69.14	68.95	68.98	68.98	
$\text{H}_6$	3.45	3.88	4.04	4.11	3.79	3.80	3.78	
$\text{O}_6$	27.59	27.03	26.81	26.75	27.26	27.22	27.20	
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	
	100.00	100.00	100.00	100.00	100.00	100.00	99.96	

Schunck has also submitted hydrated alizarine to analysis; it lost on desiccation 18.3 p. c. of water, which, when calculated upon the above formula, corresponds nearly to 4 equivalents of water, calculated (17.1 p. c.). The composition of hydrated alizarine is, therefore,



Equivalent.	Calc.	Found. (Schunck).		
$\text{C}_{20}$	57.14	58.97	56.94	57.02
$\text{H}_{10}$	4.76	4.19	5.13	5.87
$\text{O}_{10}$	38.10	—	—	—
	<hr/>			
	100.00			

The amount of carbon found corresponds exactly with the calculated number; the discrepancy in the amounts of hydrogen found arises from the use of warm chromate of lead in the first analysis, while in the two latter the substance was even mixed in a cold mortar.

The composition of the compounds obtained by precipitating an ammoniacal solution of alizarine with chloride of calcium and chloride of barium, and when dried at 100°, corresponds to the following formula :

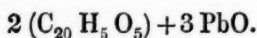
*Lime-compound* . . .  $2(C_{20}H_6O_6) + 3(CaO.HO)$

	Calc.	Found.	(Schunck.)
Percentage of lime . .	18·3	18·30	18·58

*Baryta-compound* . . .  $2(C_{20}H_6O_6) + 3(BaO.HO)$

	Calc.	Found.
Percentage of baryta . .	38·0	38·03

Schunck's lead-compound corresponds most nearly with the formula,

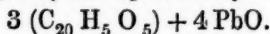


	Calc.	Found (Schunck).	
Carbon . . . . .	36·1	37·5	36·9
Hydrogen . . . . .	1·5	1·7	1·6
Oxygen . . . . .	12·1	—	—
Protoxide of lead . . .	50·3	49·1	49·8

---

100·0

The lead-compound, analysed by Debus, contains the alizarine and protoxide of lead in another proportion, which (when the substance is dried at 120°) may be expressed by the formula,



	Calc.	Found (Debus).	
Carbon . . . . .	38·2	38·18	38·51
Hydrogen . . . . .	1·6	1·97	1·98
Oxygen . . . . .	12·8	—	—
Protoxide of lead . . .	47·4	47·62	—

---

100·0

Of the products of decomposition of alizarine, one only is accurately known, that namely which is produced by various oxidizing agents, and has been described by Schunck under the name of *Alizaric acid*. Laurent and Gerhardt\* have recently pointed out the close correspondence of alizaric acid, in its properties and composition, with *Phtalic acid*. By treating garancine with nitric acid, these chemists obtained an acid, the ammonia-salt of which yielded, on sublimation, a substance similar to phtalimide in all its properties.

\* Compt. Rend. par Gerhardt et Laurent, 1849, 222.

Hence they are of opinion that no doubt can exist with respect to the identity of alizaric and phthalic acids.

I am enabled to quote some quantitative determinations which prove the identity of the acid obtained from alizarine and of phthalic acid. I am indebted to Professor Liebig for a specimen of alizaric acid, prepared by Schunck himself. It accords perfectly in its physical properties with the acid obtained from naphthaline. The silver-salt of the acid, dried at  $100^{\circ}$ , furnished, on analysis, the following numbers:

- I. 0.4465 grms. of the salt, burnt with chromate of lead, gave:  
 0.4195 " " carbonic acid, and  
 0.0455 " " water.  
 II. 0.4475 " " gave, on careful ignition :  
 0.2540 " " of silver.  
 III. 0.5443 " " gave :  
 0.3090 " " of silver.

The silver-salt explodes when rapidly heated; this may be avoided by heating it gently and lighting it with a piece of burning paper.

These numbers correspond, in 100 parts, with the composition of the phthalate of silver.

	Equiv.	Calculated.		Found.		
				I.	II.	III.
Carbon . .	16	96	25.3	25.6	—	—
Hydrogen .	4	4	1.0	1.1	—	—
Oxygen . .	8	64	16.9	—	—	—
Silver . .	2	216	56.8	—	56.7	56.8
	<hr/>	<hr/>	<hr/>			
	30	380	100.0			

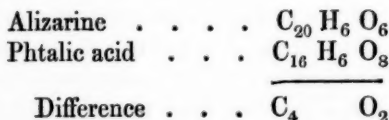
Schunck's analysis of his *alizeric acid* and *pyro-alizeric acid* (anhydrous phthalic acid) may be quoted as further proofs of the identity of the two acids.

The formula of phthalic acid is  $C_{16}H_6O_8$ , and that of anhydrous phthalic acid is  $C_{16}H_4O_6$ .

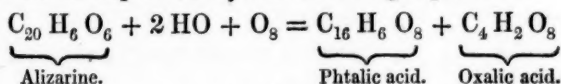
	Phthalic acid.		Anhydrous phthalic acid.	
	Calc.	Mean	Calc.	Found.
In 100 parts, $C_{16}$	57.8	57.5	$C_{16}$	64.9
" " " $H_6$	3.6	3.9	$H_4$	2.7
" " " $O_8$	38.6	—	$O_6$	32.4
	<hr/>		<hr/>	
	100.0		100.0	

If we compare the formula of alizarine with that of its product of

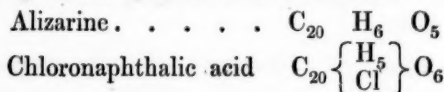
oxidation, it will be found that 4 equivalents of carbon have been eliminated and that 2 equivalents of oxygen have entered into the compound.



The 4 equivalents of carbon are probably eliminated in the form of oxalic acid, as the latter is obtained in considerable quantity in the treatment of madder with nitric acid. The decomposition of alizarine by nitric acid is expressed by the following equation :



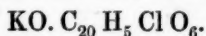
The new formula of alizarine brings to light a close connection between this colouring matter and a substance obtained by Laurent,\* in his elaborate research on the metamorphoses of naphthaline, namely, *Chloronaphthalic acid*. The latter substance is *Chlorinated Alizarine*, as will be seen by the comparison of their formulæ :



That the apparent relation exhibited by the formulæ of these substances really exists, is proved by the close analogy of their properties and products of decomposition. The acid character of alizarine is only feeble, that of chloronaphthalic acid is more strongly marked, as is generally the case with chlorinated compounds.

The *chloronaphthalic acid* of Laurent is a yellow substance, almost insoluble in water, dissolving in alcohol and ether in larger, but still not very considerable, quantity. It fuses at  $200^\circ$ , and may be sublimed without change. It dissolves in concentrated sulphuric acid without undergoing decomposition. Its combinations with metallic oxides exhibit lively colours, extending from yellow to bright red.

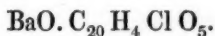
*Solution of potassa* dissolves chloronaphthalic acid with a deep red colour. A concentrated solution deposits, on cooling, a crimson salt, crystallized in needles, whose formula, according to Laurent, is :



The *ammonia-salt* is similar to the foregoing.

\* Revue Scientifique, XIII.

The *baryta-salt* is obtained by double decomposition in the form of golden-yellow needles, of silky lustre, which, when dried at  $100^{\circ}$ , have the formula,

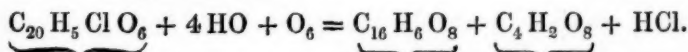


The *lime-salt* is obtained, like the other salts, by double decomposition; it crystallizes in orange-coloured needles. The *strontia-salt* has the same colour.

*Protochloride of mercury* gives a red-brown precipitate; solution of *alum* an orange-coloured; solution of *protoxide of lead* a reddish-yellow; and solution of *oxide of silver* a blood-red precipitate, becoming carmine red and crystalline when heated. Salts of the *protoxides of cobalt* and *copper* give carmine-coloured precipitates.

Chloronaphthalic acid dyes neither mordantized cloth, nor cotton mordantized or oiled for turkey red. This might have been expected, the acid character of the substance being already too strongly defined.

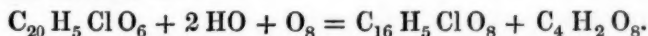
The close similarity of character between chloronaphthalic acid and alizarine—a similarity which is found only in the nearest substitution products—is further supported by the corresponding decomposition of these two substances by nitric acid. According to Laurent, chloronaphthalic acid is converted, by treatment with nitric acid, into *oxalic* and *phtalic acids*.



Chloronaphthalic acid.

Phtalic acid.      Oxalic acid.

The only difference consists in the simultaneous elimination of chlorine and its substitution by hydrogen. It is possible, however, that, instead of phtalic acid, a chlorinated phtalic acid was formed, in which case the decomposition would correspond still more closely with that of alizarine:



Laurent has also obtained, besides this chloronaphthalic acid, a *pentachloronaphthalic acid* ( $\text{C}_{20} \left\{ \begin{smallmatrix} \text{H} \\ \text{Cl}_5 \end{smallmatrix} \right\} \text{O}_6$ ), which likewise yields carmine-coloured salts insoluble in water. I have myself obtained in the preparation of naphthalic acid, an acid which did not yield with solution of baryta, the usual golden-yellow baryta-salt, but a splendid purple-red compound. I had too small a quantity of substance at my command for an analysis; it was probably a bi- or terchloronaphthalic acid. I obtained, simultaneously with this substance, a *chlorinated phtalic acid*, which has not been described

hitherto. I prepared the potassa-salt of this acid by saturating a boiling alcoholic solution with solution of potassa; it quickly separated in small plates of silvery lustre, which, when dried at  $140^{\circ}$ , gave, on analysis, the following numbers:

0.4045	grm. of potassa-salt gave:
0.2175	„ „ sulphate of potassa.
0.3495	„ „ potassa-salt, burnt with chromate of lead, gave:
0.3890	„ „ carbonic acid, and
0.0215	„ „ water.

These determinations correspond with the composition of *bichlorophthalate of potassa*.

	Calc.	Found.
C <sub>16</sub> . . .	30.8	30.4
H <sub>2</sub> . . .	0.6	0.7
Cl <sub>2</sub> . . .	22.8	—
O <sub>8</sub> . . .	20.6	—
K <sub>2</sub> . . .	25.1	24.3
	<hr/> 100.0	

The question now arose whether it would be possible to expel the one equivalent of chlorine from chloronaphthalic acid and to replace it by hydrogen.

Two methods in particular are known for obtaining the original substance from chlorinated compounds. Melsens\* reconverted *chloracetic* into *acetic acid* by the action of potassium-amalgam, (1 of potassium to 150 of mercury). The potassium dissolves without evolution of gas, as long as any chlorine is contained in the organic substance, in place of which hydrogen is taken up. Kolbe† made use of the galvanic current for the same purpose, and with great success; he passed the current into the neutral liquid by means of two amalgamated zinc plates.

I have endeavoured to obtain alizaric acid from chloronaphthalic acid by both these methods, without however arriving at the desired result. If potassium-amalgam is brought in contact with chloronaphthalic acid and water, the liberated potassa soon dissolves the acid, forming a dark red liquid, which however never exhibits the blue colour of the alizarine solution by reflected light. After a time, the solution contained chloride of potassium, and the colour of the solution diminished in intensity. A yellow precipitate was obtained

\* Ann. Ch. Phys. [3] X, 233.

† Ann. Ch. Pharm. LIV, 274.

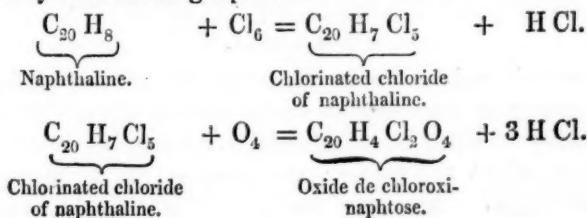


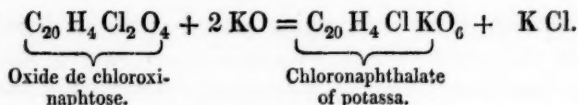
by the addition of an acid, which proved to be unaltered chloronaphthalic acid, as it yielded, with solution of baryta, the beautiful golden-coloured needles already mentioned. A portion of the acid had undergone a decomposition, which was however not limited to the substitution of hydrogen for the atom of chlorine, but had at once proceeded further.

The insolubility of chloronaphthalic acid in slightly acidulated water precluded its decomposition in such a solution by the galvanic current. When subjected to the current in an alkaline solution, chloronaphthalic acid soon underwent a change, which was indicated by the decrease in the colour of the solution and the assumption of a brown coloration, as also by the presence of chlorine in the liquid. But in this case likewise, no alizarine could be detected at any period of the operation.

Although these experiments have led to no positive results, I have no doubt that continued exertions and the application of new agents, will lead to a reaction, the results of which will be more within reach of the means presented to us by the science.

Chloronaphthalic acid was prepared by Laurent, by treating the compound  $C_{20}H_7Cl_5$  (*chlorure de chloronaphtase*) with nitric acid. Chlorine is passed over naphthaline, until the mass, at first in a state of fusion, has assumed an unctuous consistence, when the chloride of naphthaline is dissolved out by ether, and obtained, by evaporation of the ether, in the form of an oily liquid. This is submitted for several days to a current of chlorine, the resulting viscid matter being rendered more fluid, towards the end of the operation, by the application of heat. After the action is complete, the substance is dissolved in boiling ether, which, on cooling, deposits the chlorinated chloride of naphthaline; this is boiled with nitric acid till it no longer solidifies on cooling, but remains in the form of a viscid mass. A yellow powder is separated by the addition of ether, to which Laurent has given the name *oxyde de chloroxinaphtose*. When treated with an alcoholic solution of potassa, this substance is immediately converted into chloronaphthalic acid. These reactions may be expressed by the following equations:





Now it is evident that, if chloride of naphthaline ( $\text{C}_{20}\text{H}_8\text{Cl}_4$ ) were to be submitted to these reactions, the final product would also contain 1 equivalent of chlorine less and 1 equivalent of hydrogen more; in fact, alizarine ( $\text{C}_{20}\text{H}_6\text{O}_6$ ) must then be obtained instead of  $\text{C}_{20}\text{H}_5\text{ClO}_6$ . In the treatment of the chlorinated chloride of naphthaline by nitric acid, a large quantity of the substance is converted into further products of decomposition, namely into phthalic and oxalic acids. The chlorinated compounds withstand the oxidizing action of nitric acid much better than the normal substances, and this may be the reason why chloride of naphthaline yields, instead of  $\text{C}_{20}\text{H}_6\text{O}_6$ , only the products of decomposition of that substance, namely phthalic and oxalic acids. The experiments of Schunck have shown that alizarine, when boiled with nitric acid, splits up readily into phthalic and oxalic (?) acids.

I do not know whether I shall be able to follow up this subject; I believe, however, to have pointed out with sufficient clearness in the foregoing, the manner in which we may hope to obtain alizarine from naphthaline. The method would be to check the reaction at a certain point; this might be arrived at by the employment of a more feeble oxidising agent than nitric acid, as the latter always effects a further decomposition.

The theoretical and practical interest of the above question leads me to hope that chemists will bestow a little attention upon it. If it be considered, that, according to the experiments of Robiquet and Schunck, alizarine not only produces the same colours as madder, but even possesses advantages over the raw material; if, besides this, the small amount of alizarine required for dyeing, and the low price of naphthaline, obtained as it is in large quantities in the manufacture of coal-gas, be taken into consideration, it will be evident that, even if a very elaborate and circuitous method should be requisite for the conversion of naphthaline into alizarine, its practical application might still be found advantageous.

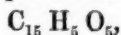
#### PURPURINE.

This second red colouring principle of madder differs from alizarine chiefly by its solubility in solution of alum. If a concentrated solution of alum be boiled with purpurine, the latter dissolves with a fine bright red colour; the solution has an orange colour by reflected light. Ammonia precipitated a red-lake, varying in

colour, when dry, from rose to *ponceau*, according to the quantity of alumina present. The solubility of purpurine in solution of alum has been applied by Runge and Debus to the separation of this substance from alizarine. Purpurine differs in appearance according to the conditions under which it crystallizes. It is deposited from its solution in strong alcohol, in red needles, and from weak spirits in thin, soft, orange-coloured needles, forming a matted mass, when dried. These orange-coloured crystals contain water of crystallization, which they part with at  $100^{\circ}$ , assuming a red colour. A specimen of pure purpurine, containing, however, some red crystals (anhydrous purpurine) in admixture, lost 4.9 of water at  $120^{\circ}$ . Runge describes his purpurine as occurring in orange-coloured crystallized grains, and Debus his oxylicaric acid as forming red needles, from  $\frac{1}{6}$  to  $\frac{1}{8}$  of an inch in length. Purpurine is more easily soluble in warm water than alizarine, and forms a red solution. It fuses when heated, and sublimes with deposition of carbon. Its solution in alcohol has likewise a much deeper red colour than that of alizarine; it dissolves in ether and in concentrated sulphuric acid. Purpurine\* may be easily distinguished from alizarine by the colour of its solution in potassa; it is bright red, and does not possess the blue tint characteristic of alizarine. Purpurine gives purple-coloured precipitates with lime- and baryta-salts, which are easily distinguishable from those of alizarine. The lead-compound is likewise purple. Purpurine is also insoluble in a concentrated solution of carbonate of soda in the cold; it dissolves on ebullition, but separates again perfectly from the solution on cooling. The compound of purpurine with potassa- (?) alkali is also insoluble in other salt-solutions.

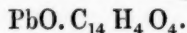
Runge has already shown that purpurine dyes cloth purple when mordantized with alumina, rose-coloured with tin-mordant, ponceau-coloured with lead-mordant, and violet with iron-mordant. I have convinced myself that purpurine imparts to stuffs mordantized with alumina, as well as to cotton which has been oiled and mordantized for turkey-red, a fine deep red dye without any blue tint, and that these colours are not altered by the process of raising with soap. It cannot, therefore, be doubted that purpurine plays a part in turkey-red dyeing, as well as in the common-madder dyeing.

Debus has published several concordant analyses of purpurine (oxylicaric acid), which correspond exactly to the formula,



\* I am not able to confirm the statement made by Schiel, that sublimed madder-purple (purpurine) dissolves with a blue colour in solution of potassa. Purpurine, repeatedly sublimed, dissolved in potassa with a bright red colour.

To a lead-compound of purpurine, he has assigned the formula,



It has already been seen, with alizarine, how little reliance can be placed on the atomic weights derived from compounds of bodies like these, of feebly acid properties; the equivalent proportion  $\text{C}_8 \text{H}_2 \text{O}_4$ , determined upon by Debus seems, however, undoubtedly correct, and the most probable formula appears to be  $\text{C}_{18} \text{H}_6 \text{O}_6$ . Hydrated purpurine would contain, according to the above determination, one equivalent of water of crystallization (calc. 5.3 per cent).

A certain connection between two substances, occurring in the same plant and so similar in properties to each other, might reasonably be expected. Debus interpreted the composition of alizarine and purpurine, as found by him, by assuming the presence of one atom more of oxygen in the former than in the latter; the endeavours to convert alizarine into purpurine by the action of oxygen, were not attended with the expected result. The following experiment would however seem to indicate a reconversion of alizarine into purpurine. Some madder from Elsars was suspended in water, mixed with fresh yeast, and kept for some time in a closed vessel at a temperature of about  $30^\circ$ . Fermentation was soon set up, as was indicated by the brisk evolution of carbonic acid. After the lapse of two days, the action terminated—the liquid was powerfully acid—and, when distilled, yielded alcohol and a trace of a volatile acid; the strongly acid residue contained much phosphoric acid.

The liquid was separated from the solid portion by a cloth; the solid matter removed, and treated with a boiling solution of alum, which assumed the exact colour of purpurine. On cooling, the solution deposited, besides crystallized alum, a red colouring matter, which dissolved again when boiled with more solution of alum, and contained, besides purpurine, a mere trace of alizarin. The addition of sulphuric acid to the alum-solution separated a considerable quantity of purpurine, which, after extraction with boiling hydrochloric acid, yielded from its alcoholic and ethereal solutions crystals of purpurine mixed with an amorphous substance. The alizarine appeared therefore to have disappeared, while a considerable quantity of purpurine was obtained. It would, however, be necessary, in order to prove decidedly whether alizarine is converted into purpurine by fermentation to submit pure alizarine mixed with yeast to fermentation.

## ABSTRACTS

OF

### PAPERS IN THE "PHILOSOPHICAL TRANSACTIONS."

By HENRY WATTS, B.A., F.C.S.

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#### On the Diffusion of Liquids.

By Professor Graham.\*

Any saline or other soluble substance, once liquefied and in a state of solution, is evidently spread or diffused uniformly through the mass of the solvent by a spontaneous process.

It has often been asked whether this process is of the nature of the diffusion of gases; but no satisfactory answer to the question appears to be obtained, owing, it is believed, to the subject having been studied chiefly in the operations of endosmose, where the action of diffusion is complicated and obscured by the imbibing power of the membrane, which is peculiar for each soluble substance, but no way connected with the diffusibility of the substance in water. Hence also it was not the diffusion of the salt, but rather the diffusion of the solution, which was generally regarded. A diffusibility like that of gases, if it exists in liquids, should afford means for the separation and decomposition even of unequally diffusible substances, and being of a purely physical character, the necessary consequence and index of *density*, should present a scale of densities for substances in the state of solution, analogous to vapour-densities, which would be new to molecular theory.

M. Gay-Lussac proceeded upon the assumed analogy of liquid to gaseous diffusion, in the remarkable explanation which he suggested of the cold produced on diluting certain saline solutions, namely, that the molecules of the salt expand into the water like a compressed gas admitted into additional space.

The phenomena of solubility at the same time were considered by that acute philosopher as radically different from those of chemical affinity, and as the result of an attraction which is of a physical or mechanical kind. The characters indeed of these two attractions are strongly contrasted. Chemical combination is uniformly attended with the evolution of heat, while solution is marked with equal

\* Phil Trans. 1850, I, 1.

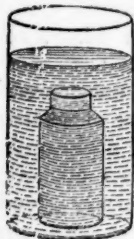
constancy by the production of cold. The substances which combine chemically are the dissimilar, while the soluble substance and its solvent are the like or analogous in composition and properties.

In the consideration of solubility, attention is generally engrossed entirely by the quantity of salt dissolved. But it is necessary to apprehend clearly another character of solution, namely, the degree of force with which the salt is held in solution, or the intensity of the solvent attraction, quite irrespective of quantity dissolved. In the two solid crystalline hydrates, pyrophosphate of soda and sulphate of soda, we see the same ten equivalents of water associated with both salts, but obviously united with unequal degrees of force, the one hydrate being persistent in dry air, and the other highly efflorescent. So also in the solutions of two salts, which are equally soluble in point of quantity, the intensity of the attraction between the salt and the water may be very different, as exemplified in the large but feeble solubility in water of such bodies as the iodide of starch or the sulphindylate of potash, compared with the solubility of hydrochloric acid or of the acetate of potash, which last two substances are capable of precipitating the two former, by displacing them in solution. Witness also the unequal action of animal charcoal in withdrawing different salts from solution, although the salts are equally soluble; and the unequal effect upon the boiling-point of water produced by dissolving in it the same weight of various salts. Besides being said to be small or great, the solubility of a substance has also therefore to be described as weak or strong.

The gradations of intensity observed in the solvent force are particularly referred to, because the inquiry may arise how far these gradations are dependent upon unequal diffusibility; whether indeed rapidity of diffusion is not a measure of the force in question.

A number of six-ounce phials were first made use of to contain the solutions, and to form what are called the Solution phials or cells. They were of the same make, and selected from a large stock, of the common aperture of 1.175 inch. Both the mouths and bottoms of these phials were ground flat. The mode of making an experiment

FIG. 1.



and the apparatus (Fig. 1.) have already been described in a paper by the author, "On the Application of Liquid Diffusion to produce Decomposition."\*

The characters of liquid diffusion were first examined in detail in the case of chloride of sodium.

(1.) Do different proportions of chloride of sodium in solution give corresponding amounts of diffused salt?

Solutions were prepared of chloride of sodium in the proportion of 100 water with 1, 2, 3 and 4 parts of the salt.

The diffusion of all the solutions was continued

\* Chem. Soc. Qu. J. III, 60.



for the same time, eight days, at the mean temperature of  $52^{\circ}5$  Fahr.

Proportion of salt to 100 water in solution to be diffused.	Diffusion-product.	
	Ingrai ns.	Ratio.
1	2.78	1.
2	5.54	1.99
3	8.37	3.01
4	11.11	4.00

The quantities diffused appear, therefore, to be closely in proportion (for this salt) to the quantity of salt in the diffusing solution.

The relation which appears in these results is also favourable to the accuracy of the method of experimenting pursued. The variation from the speculative result does not in any observation exceed 1 per cent.

(2.) Is the quantity of salt diffused affected by temperature ?

The diffusion of the same solutions of chloride of sodium was repeated at two new temperatures,  $39^{\circ}6$  and  $67^{\circ}$ , the one being above and the other below the preceding temperature. It was necessary to use artificial means to obtain the low temperature, owing to the period of the season. A close box of double walls was employed, masses of ice being laid on the floor of the box, and the water-jars supported on a shelf above. The water and solution were first cooled separately for twenty-four hours in the ice-box, before the diffusion was commenced. It was found that the temperature could be maintained within a range of  $2^{\circ}$  or  $3^{\circ}$  for eight days. It was doubtful, however, whether the temperature was constantly the same to a degree or two in all the jars ; and the results obtained at an artificial temperature were always less concordant and sensibly inferior in precision to observations made at the atmospheric temperature.

#### DIFFUSION OF CHLORIDE OF SODIUM.

Proportion of salt to 100 water.	Diffusion-product.	
	In grains.	Ratio.
1 at $39^{\circ}6$	2.63	1.
2 " "	5.27	2.00
3 " "	7.69	2.32
4 " "	10.00	3.80
1 at $67^{\circ}$	3.50	1.
2 " "	6.89	1.97
3 " "	9.90	2.83
4 " "	13.60	3.89

The proportionality in the diffusion is still well-preserved at the different temperatures. The deviations are indeed little, if at all, greater than might be occasioned by errors of observation. The ratio of diffusion, for instance, from the solutions containing 4 parts of salt, is 3.80 and 3.89 for the two temperatures, which numbers fall little short of 4.

The diffusion manifestly increases with the temperature, and as far as can be determined by three observations, in direct proportion to the temperature. The diffusion-product from the 4 per cent. solution increases from 10 to 13.60 grs., with a rise of temperature of  $27^{\circ}4$ , or rather more than one-third. Supposing the same progression continued, the diffusibility of chloride of sodium would be doubled by a rise of 84 or 85 degrees.

(3). The progress of the diffusion of chloride of sodium in experiments of the kind narrated, was further studied by intercepting the operation after it had proceeded for different periods of 2, 4, 6 and 8 days. The solution employed was that containing 4 parts of salt to 100 water. Two of the six-ounce phials were diffused at the same time for each period.

Diffused in 1st two days . . . . .	3.95 grs.
„ 2nd „ . . . . .	3.00 „
„ 3rd „ . . . . .	2.91 „
„ 4th „ . . . . .	3.26 „

The diffusion appears to proceed pretty uniformly, if the amount diffused in the first period of two days be excepted. Each of the phials contained at first about 108 grs. of salt, of which the maximum quantity diffused is 13.12 grs. in eight days, or  $\frac{1}{8.24}$  of the whole salt. Still the diffusion must necessarily follow a diminishing progression, which would be brought out by continuing the process for a longer time, and appear at the earliest period in the salt of most rapid diffusion.

All the experiments which follow, being made like the preceding on comparatively large volumes of solution in the phial, and for equally short periods of seven or eight days, may be looked upon as exhibiting pretty accurately the initial diffusion of such solutions, the influence of the diminishing progression being still small. The volume of water in the water-jar is also relatively so large, that the experiment approaches to the condition of diffusion into an Unlimited Atmosphere.

*Diffusion of various salts and other substances.*—In the following experiments, the diffusion took place at a temperature ranging from  $62^{\circ}$  to  $59^{\circ}$ , mean  $60^{\circ}5$ , and was continued for a period of eight days; the proportion of salt in solution to be diffused being always 20 salt to 100 water, or 1 to 5. The density of the solutions is added.

DIFFUSION OF SOLUTIONS OF 20 SALT TO 100 WATER; AT 60°·5 FOR EIGHT DAYS.

Name of salt.	Density of solution at 60°.	Anhydrous salt diffused.	
		In grains.	Means.
Chloride of sodium . . . .	1·1265	58·5	
Chloride of sodium . . . .	1·1265	58·87	58·68
Sulphate of magnesia . . . .	1·185	27·42	27·42
Nitrate of soda . . . . .	1·120	52·1	
Nitrate of soda . . . . .	1·120	51·02	51·56
Sulphate of water . . . . .	1·108	68·79	
Sulphate of water . . . . .	1·108	69·86	69·32
Crystallized cane-sugar. . . .	1·070	26·74	26·74
Fused cane-sugar . . . . .	1·066	26·21	26·21
Starch-sugar (glucose) . . . .	1·061	26·94	26·94
Treacle of cane-sugar . . . .	1·069	32·55	32·55
Gum-arabic . . . . .	1·060	13·24	13·24
Albumen . . . . .	1·053	3·08	3·08

The following additional ratios of diffusion were obtained from similar solutions at a somewhat lower temperature, namely 48°;—chloride of sodium 100; hydrate of potash 151·93; ammonia (from a 10 per cent solution, saturated with chloride of sodium to increase its density) 70; alcohol (saturated with chloride of sodium) 75·74; chloride of calcium 71·23; acetate of lead 45·46.

Where two experiments upon the same salt are recorded in the table, they are seen to correspond to within 1 part in 40, which may be considered as the limit of error in the present observations. It will be remarked that the diffusion of cane- and starch-sugar is sensibly equal, and double that of gum-arabic. On the other hand, the sugars have less than half the diffusibility of chloride of sodium. It is remarkable that the specifically lightest and densest solutions, those of the sugars and of sulphate of magnesia, approach each other closely in diffusibility. On comparing together, however, two substances of similar constitution, such as the two salts, chloride of sodium and sulphate of magnesia, that salt appears to be least diffusive of which the solution is densest.

But the most remarkable result is the diffusion of albumen, which is low out of all proportion when compared with saline bodies. The solution employed was the albumen of the egg, without dilution, but strained through calico and deprived of all vesicular matter. As this liquid, with a density of 1·041, contained only 14·69 parts of dry matter to 100 of water, the proportion diffused is increased in the table to that for 20 parts, to correspond with the other substances. In its natural alkaline state, the albumen is least diffusive,

but when neutralized by acetic acid, a slight precipitation takes place, and the liquid filters more easily. The albumen is now sensibly more diffusive than before. Chloride of sodium appears twenty times more diffusible than albumen in the table, but the disparity is really greater; for nearly one-half of the matter which diffused from the latter consisted of inorganic salts. Indeed, the experiment appears to promise a delicate method of proximate analysis peculiarly adapted for animal fluids. The value of this low diffusibility in retaining the serous fluids within the blood-vessels at once suggests itself. Similar results were obtained with egg-albumen, previously diluted and well-beaten with 1 and 2 volumes of water.

Nor does albumen impair the diffusion of salts dissolved together with it in the same solution, although the liquid retains its viscosity. Three other substances, added separately in the proportion of 5 parts to 100 of the undiluted solution of egg-albumen, were found to diffuse out quite as freely from that liquid as they did from an equal volume of pure water: these were chloride of sodium, urea and sugar. Urea proved to be a highly diffusible substance. It nearly coincided in rate with chloride of sodium.

A second series of salts were diffused containing 1 part of salt to 10 of water—a smaller proportion of salt which admits of the comparison of a greater variety of salts. The temperature during the period of eight days was remarkably uniform, 60°—59°.

DIFFUSION OF SOLUTIONS OF 10 SALT TO 100 WATER AT 59°·5.

Name of salt.	Density of solution at 60°.	Anhydrous salt diffused.	
		In grains.	Means.
Chloride of sodium . . . .	1·0668	32·3	
Chloride of sodium . . . .	1·0668	32·2	32·25
Nitrate of soda . . . . .	1·0622	30·7	30·7
Chloride of potassium . . .	1·0596	40·15	40·15
Chloride of ammonium . . .	1·0280	40·20	40·20
Nitrate of potash . . . . .	1·0589	35·1	
Nitrate of potash . . . . .	1·0589	36·0	35·55
Nitrate of ammonia . . . .	1·0382	35·3	35·3
Iodide of potassium . . . .	1·0673	37·0	37·0
Chloride of barium . . . . .	1·0858	27·0	27·0
Sulphate of water . . . . .	1·0576	37·18	
Sulphate of water . . . . .	1·0576	36·53	36·85
Sulphate of magnesia . . . .	1·0965	15·3	
Sulphate of magnesia . . . .	1·0965	15·6	15·45
Sulphate of zinc . . . . .	1·0984	15·6	
Sulphate of zinc . . . . .	1·0984	16·0	15·80

Before adverting to the relations in diffusibility which appear to exist between certain salts in the preceding table, the results of the diffusion of the same solutions at a lower temperature may be stated.

DIFFUSION OF SOLUTIONS OF 10 SALT TO 100 WATER AT 37°5.

Name of salt.	Anhydrous salt diffused.	
	In grains.	Means.
Chloride of sodium . . . .	22·21	
Chloride of sodium . . . .	22·74	22·47
Nitrate of soda . . . . .	22·53	
Nitrate of soda . . . . .	23·05	22·79
Chloride of ammonium . . . .	31·14	31·14
Nitrate of potash . . . . .	28·84	
Nitrate of potash . . . . .	28·56	28·70
Nitrate of ammonia . . . . .	29·19	29·19
Iodide of potassium . . . . .	28·10	28·10
Chloride of barium . . . . .	21·42	21·42
Sulphate of water . . . . .	31·11	
Sulphate of water . . . . .	28·60	29·85
Sulphate of magnesia . . . .	13·03	
Sulphate of magnesia . . . .	13·11	13·07
Sulphate of zinc . . . . .	11·87	
Sulphate of zinc . . . . .	13·33	12·60

The near equality of the quantities diffused of certain isomorphous salts is striking at both temperatures. Chloride of potassium and chloride of ammonium give 40·15 and 40·20 grs. respectively in the first table. Nitrate of potash and nitrate of ammonia 35·55 (mean) and 35·3 grs. respectively in the first table, and 28·70 and 29·19 grs. in the second table. Sulphate of magnesia and sulphate of zinc 15·45 and 15·8 grs. (means) in the first table, with 13·07 and 12·60 grs. in the second. The relation observed is the more remarkable, that it is that of equal weights of the salts diffused, and not of atomically equivalent weights. In the salts of ammonia and potash, this equality of diffusion is exhibited also, notwithstanding considerable differences in density between their solutions; the density of the solution of chloride of ammonium, for instance, being 1·0280, and that of chloride of potassium 1·0596. It may have some relation however, but not a simple one, to the density of the solutions; sulphate of magnesia, of which the solution is most dense, being most slowly diffusive; and salts of soda being slower, as they are generally denser in solution, than the corresponding salts of potash. Nor does it depend upon equal solubility, for in none of the pairs is there any approach to equality in that respect.

A comparison was now made of the diffusibility of several acids, diffused from 4 per cent solutions, from which it appeared that hydrochloric and nitric acids were sensibly equal, and had a diffusibility nearly double that of sulphuric acid. The diffusion of chloride of sodium being 13·32 grs., that of hydrochloric acid was 34·1, of nitric acid 33·5, of sulphuric acid 18·48, of oxalic acid 12·38, and of tartaric acid 9·79.

*Diffusion of ammoniated salts of copper.*—It was interesting to compare together such related salts as sulphate of copper, the ammoniated sulphate of copper, or soluble compound of sulphate of copper with 2 equivs. of ammonia, and the sulphate of ammonia. It is well known that metallic oxides, or subsalts of metallic oxides, when dissolved in ammonia and the fixed alkalis, are easily taken down by animal charcoal. This does not happen with the ordinary neutral salts of the same acids, which are held in solution by a strong attraction. Supposing the existence of a scale of the solvent attraction of water, the preponderance of the charcoal attraction will mark a term in that scale. And if the solvent force is nothing more than the diffusive tendency, it will follow that salts which can be taken down by charcoal must be less diffusible than those which cannot.

Of sulphate of ammonia and of sulphate of copper solutions were prepared, consisting of 4 anhydrous salt to 100 water, the sulphate of ammonia being of course taken as  $\text{NH}_4\text{O}.\text{SO}_3$ . The solution of the copper-salt was divided into two portions, one of which had caustic ammonia added to it in slight excess, so as to produce the azure blue solution of ammonio-sulphate of copper.

The solutions were diffused for eight days, at a mean temperature of 64°·9 for the sulphates and nitrates, and 67°·7 for the chlorides.

DIFFUSION OF SOLUTIONS, 4 SALT TO 100 WATER.

Name of salt.	Density of solution at temperature of experiment.	Anhydrous salt diffused in grains. Mean of 2 expts.
Sulphate of ammonia . . . . .	1·0235	12·05
Sulphate of copper . . . . .	1·0369	6·35
Ammonio-sulphate of copper . . . . .	1·0308	1·44
Nitrate of ammonia . . . . .	1·0136	15·80
Nitrate of copper . . . . .	1·0323	9·77
Ammonio-nitrate of copper . . . . .	1·0228	1·56
Chloride of ammonium . . . . .	1·0100	16·19
Chloride of copper . . . . .	1·0328	10·65
Ammonio-chloride of copper . . . . .	1·0209	4·24

It will be observed that the quantity of sulphate of copper diffused out in the experiments falls from 6·35 in the neutral salt to 1·44 grs.



in the ammoniated salt; of nitrate of copper from 9.77 to 1.56, and of chloride of copper from 10.65 to 4.24. These numbers are to be taken only as approximations; they are sufficient, however, to prove a much reduced diffusibility in the ammoniated salts of copper.

*Diffusion of mixed salts.*—When two salts can be mixed without combining, it is to be expected that they will diffuse separately and independently of each other, each salt following its special rate of diffusion.

(1). Anhydrous sulphate of magnesia and sulphate of water (oil of vitriol), 1 part of each, were dissolved together in 10 parts of water, and the solution allowed to diffuse for four days at 61°5.

The water-jar was found to have acquired:

Sulphate of magnesia . . . .	5.60 grs.
Sulphate of water . . . . .	21.92 „

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27.52 grs.

(2). A solution was also diffused of 1 part of anhydrous sulphate of soda and 1 part of chloride of sodium in 10 parts of water, for four days at 61°5. The salt which diffused out in that time consisted of:

Sulphate of soda . . . . .	9.48 grs.
Chloride of sodium . . . . .	17.80 „

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27.28 grs.

The sulphate of soda in the last experiment had begun to crystallize in the solution-phial, from a slight fall of temperature, before the diffusion was interrupted, a circumstance which may have contributed to increase the inequality of the proportions diffused of the mixed salts.

(3). A solution of equal weights of anhydrous carbonate of soda and chloride of sodium, namely, of 4 parts of the one salt and 4 parts of the other to 100 water, was diffused from three four-ounce phials of 1.25 inch aperture, at a mean temperature of 57°9 and for seven days. The diffusion product amounted to 17.10, 17.58, and 18.13 grs. of mixed salt in the three experiments. The analysis of the last product of 18.13 grs. gave:

Carbonate of soda . . . . .	5.68	31.33
Chloride of sodium . . . . .	12.45	68.67
	<hr/>	<hr/>
	18.13	100.00

The least soluble of the two salts appears in all cases to have its diffusibility lessened in the mixed state. The tendency to crystallization of the least soluble salt must evidently be increased by the admixture. Now it is this tendency, or perhaps more generally the

increased attraction of the particles of salt for each other, when approximated by concentration, which most resists the diffusion of a salt, and appears to weaken the diffusive force in mixtures, as it is also found to do so in a concentrated solution of a single salt.

(5). The salt which diffused from a strong solution of sulphates of zinc and magnesia, consisting of 1 part of each of these salts in the anhydrous state and 6 parts of water, did not consist of the two salts in exactly equal proportions. The mixture of salts, diffused for eight days, as in the late experiments, gave the following results :

	Exp. I.	II.	III.
Sulphate of zinc . . . .	8.12	7.49	8.12
Sulphate of magnesia . . .	8.68	8.60	8.75
	<hr/> 16.80	<hr/> 16.09	<hr/> 16.87

There is, therefore, always a slight but decided preponderance of sulphate of magnesia, the more soluble salt, in the diffusion-product.

It appears from all these experiments, that the inequality of diffusion which existed is not diminished but exaggerated in mixtures, a curious circumstance, which has also been observed of mixed gases.

*Separation of salts of different bases by diffusion.*—It was now evident that inequality of diffusion supplies a method for the separation, to a certain extent, of some salts from each other, analogous in principle to the separation of unequally volatile substances by the process of distillation. The potash-salts appearing to be always more diffusive than the corresponding soda-salts, it follows, that if a mixed solution of two such salts be placed in the solution phial, the potash-salt should escape into the water atmosphere in largest proportion, and the soda-salt be relatively concentrated in the phial. This anticipation was fully verified.

(1). A solution was prepared of equal parts of the anhydrous carbonates of potash and soda in 5 times the weight of the mixture of water. Diffused from a small thousand-grain phial of 1.1 inch aperture, into 6 ounces of water, for nineteen days, at a temperature above 60°, it gave a liquid of density 1.0350, containing a considerable quantity of the salts, in the proportion of :

Carbonate of soda . . . .	36.37
Carbonate of potash . . . .	63.63
	<hr/> 100.00

A partial separation of the salts of sea-water was effected in a similar manner.

(2). The sea-water (from Brighton) was of density 1.0265. One thousand grs. of the liquid yielded 35.50 grs. of dry salts, of which

2.165 grs. were magnesia. The dry salts contain therefore 6.10 per cent of that earth.

Six thousand-grain phials, of 1.1 inch aperture, were properly filled with the sea-water and placed in six tumblers, each of the last containing 6 ounces of water. Temperature about 50°. The diffusion was interrupted after eight days. The salts of the sea-water were now found to be divided as follows:

Diffused into the tumblers . .	92.9 grs., or	36.57
Remaining in the phials . .	161.1 grs., or	63.43
	<hr/>	<hr/>
	254.0	100.00

Rather more than one-third of the salts has therefore been transferred from the solution-phials to the water-jars by diffusion.

Of the diffused salts in the tumblers, 46.5 grs. were found to contain 1.90 gr. magnesia, or 4.09 per cent. Hence the following result:

Magnesia originally in salts of sea-water . .	6.01 per cent.
Magnesia in salts diffused from sea-water . .	4.09 per cent.

The magnesia, also, must in consequence be relatively concentrated in the liquid remaining behind in the phials.

A probable explanation may be drawn from the last results of the remarkable discordance in the analysis of the waters of the Dead Sea, made by different chemists of eminence. The relative proportion of the salts is referred to, and not their absolute quantity, the last necessarily varying with the state of dilution of the saline water when taken up. The lake in question falls in level 10 or 12 feet every year, by evaporation. A sheet of fresh water of that depth is thrown over the lake in the wet season, which water may be supposed to flow over a fluid nearly 1.2 in density, without greatly disturbing it. The salts rise from below into the superior stratum of fresh water by the diffusive process, which will bring up salts of the alkalis with more rapidity than salts of the earth, and chlorides, of either class, more rapidly than sulphates. The composition of water near the surface must therefore vary greatly, as this process is more or less advanced.

Chemical analysis, which gives with accuracy the proportions of acids and bases in a solution, furnishes no means of deciding how these acids and bases are combined, or what salts exist in solution. But it is possible that light may be thrown on the constitution of mixed salts, at least when they are of unequal diffusibility, by means of a diffusion experiment. With reference to sea-water, for instance, it has been a question in what form the magnesia exists, as chloride or as sulphate; or how much exists in the one form and how much in the other. Knowing, however, the different rates of diffusibility of these two salts, which is nearly chloride 3 and sulphate 2, and their rela-

tion to the diffusibility of chloride of sodium, we should be able to judge from the proportion in which the magnesia travels in company with chloride of sodium, whether it is travelling in the large proportion of chloride of magnesium, in the small proportion of sulphate of magnesia, or in the intermediate proportion of a certain mixture of chloride and sulphate of magnesia. But here we are met by a difficulty. Do the chloride of magnesium and sulphate of magnesia necessarily pre-exist in sea-water in the proportions in which they are found to diffuse? May not the more easy diffusion of chlorides determine their formation in the diffusive act, just as evaporation determines the formation of a volatile salt—producing carbonate of ammonia, for instance, from hydrochlorate of ammonia with carbonate of lime in the same solution? It was proved that liquid diffusion, as well as gaseous evaporation, can produce chemical decompositions.

*Decomposition of salts by diffusion.*—From bisulphate of potash, saturated at  $68^{\circ}$  and of density 1.280, there diffused out :

Sulphate of potash	. . .	20.37	} Bisulphate of potash.
Sulphate of water	. . .	11.47	
Sulphate of water	. . .	12.77	
<hr/>			
44.61			

It thus appears that the bisulphate of potash undergoes decomposition in diffusing, and that the acid diffuses away to about double the extent, in equivalents, of the sulphate of potash.

From a 4 per cent solution of alum at  $64^{\circ}$ , the diffusion-product was found to be :

Alum	. . . . .	5.33	71.26
Sulphate of potash	. . .	2.15	28.74
		<hr/>	<hr/>
		7.48	100.00

This otherwise stable double salt is broken up from the high diffusibility of the sulphate of potash, compared with that of the sulphate of alumina; the separate diffusibilities of these two salts were observed to be nearly as 2 to 1.

It was interesting to observe what really diffuses from the ammoniated sulphate of copper ( $\text{CuO} \cdot \text{SO}_3 \cdot 2\text{NH}_3 + \text{HO}$ ), and to find if the low diffusibility of that salt is attended with decomposition. The diffusion of the ammoniated sulphate of copper was therefore repeated from a 4 per cent. solution in the six-ounce solution phial, for eight days, at  $64^{\circ} \cdot 2$ . In evaporating the water of the jar afterwards, the ammoniated sulphate of copper present was necessarily decomposed, by the escape of ammonia, and a subsulphate of copper precipitated. The copper found, however, was estimated as neutral sulphate of

copper. The diffusion-product of two experiments may be represented as follows, in grains :

	I.	II.
Sulphate of copper . . .	0.81	0.97
Sulphate of ammonia . . .	5.46	5.53
	<hr/> 6.27	<hr/> 6.50

The abundant formation and separation of sulphate of ammonia in these experiments, prove that the ammoniated sulphate of copper is largely decomposed in diffusion.

From the diffusion of the double crystallized sulphate of magnesia and potash, compared with that of a mixture of its constituent salts, it appeared that they were different, and that double salts dissolve in water without decomposition, although the single salts may meet in solution without combining. Hence in a mixture of salts we may have more than one state of equilibrium possible. And when a salt, like alum, happens to be dissolved in such a way as to decompose it, the constituents are not necessarily reunited by subsequent mixing. Many practices in the chemical arts, which seem empirical, have their foundation probably in facts of this kind.

*Diffusion of one salt into the solution of another salt.*—It was curious and peculiarly important, in reference to the relation of liquid to gaseous diffusion, to find whether one salt A would diffuse into water already charged with an equal or greater quantity of another salt B, as a gas *a* freely diffuses into the space already occupied by another gas *b*; the gas *b* in return diffusing at the same time into the space occupied by *a*. Or whether, on the contrary, the diffusion of the salt A is resisted by B. The latter result would indicate a neutralization of the water's attraction for a second salt, which would divide entirely the phenomena of liquid from those of gaseous diffusion.

A solution of 4 parts of carbonate of soda to 100 water, of density 1.0406 was observed to diffuse with equal rapidity into a solution of 4 parts of chloride of sodium to 100 water, having the density 1.0282, as into pure water.

The same solution of carbonate of soda was diffused into a solution of sulphate of soda, containing 4 per cent, and of density 1.0352, with a small reduction in the quantity of carbonate of soda diffused, amounting to one-eighth of the whole. The sulphate of soda therefore exercised a positive interference in checking the diffusion of the carbonate to that extent. So small and disproportionate an effect, however, is scarcely sufficient to establish the existence of a mutual elasticity and resistance between these two salts.

Still it might be said, may not the diffusion of one salt be resisted by another salt which is strictly isomorphous with the first? The

diffusion of a 4 per cent. solution of nitrate of potash, however, was found not to be sensibly reduced by the presence of 4 per cent of nitrate of ammonia in the water atmosphere.

These experiments were made upon dilute solutions, and it is not at all improbable that the result may be greatly modified in concentrated solutions of the same salts, or when the solutions approach to saturation. But there is reason to apprehend that the phenomena of liquid diffusion are exhibited in the simplest form by dilute solutions, and that concentration of the dissolved salt, like compression of a gas, is often attended with a departure from the normal character.

On approaching the degree of pressure which occasions the liquefaction of a gas, an attraction appears to be brought into play, which impairs the elasticity of the gas; so, on approaching the point of saturation of a salt, an attraction of the salt-molecules for each other, tending to produce crystallization, comes into action, which will interfere with and diminish that elasticity or dispersive tendency of the dissolved salt which occasions its diffusion.

We are perhaps justified in extending the analogy a step further between the characters of a gas near its point of liquefaction and the conditions which may be assigned to solutions. The theoretical density of a liquefiable gas may be completely disguised under great pressure. Thus, under a reduction by pressure of 20 volumes into 1, while the elasticity of air is 19.72 atmospheres, that of carbonic acid is only 16.70 atmospheres, and the deviation from their normal densities is in the inverse proportion. Of salts in solution the densities may be affected by similar causes, so that although different salts in solution really admit of certain normal relations in density, these relations may be concealed and not directly observable.

The analogy of liquid diffusion to gaseous diffusion and vaporization is borne out in every character of the former which has been examined. Mixed salts appear to diffuse independently of each other, like mixed gases, and into a water-atmosphere already charged with another salt as into pure water. Salts also are unequally diffusible, like the gases, and separations, both mechanical and chemical (decompositions), are produced by liquid as well as by gaseous diffusion. But it still remains to be found whether the diffusibilities of different salts are in any fixed proportion to each other, as simple numerical relations are known to prevail in the diffusion-velocities of the gases, from which their densities are deducible.

It was desirable to make numerous simultaneous observations on the salts compared, in order to secure uniformity of conditions, particularly of temperature. The means of greatly multiplying the experiments were obtained by having the solution-phial cast in a mould, so that any number could be procured of the same form



and dimensions. The phials were of the form represented (Fig. 2.),

FIG. 2. holding about 4 ounces, or more nearly 2080 grs. of water to the base of the neck, and the mouths of all were ground down, so as to give the phial a uniform height of 3·8 inches. The mouth or neck was also ground to fit a gauge-stopper of wood, which was 0·5 inch deep and slightly conical, being 1·24 inch in diameter on the upper, and 1·20 inch on the lower surface. These are therefore the dimen-



sions of the diffusion aperture of the new solution cells. A little contrivance to be used in filling the phials with the saline solution, to a constant distance of half an inch from the surface of the lip, proved useful. It was a narrow slip of brass plate, having a descending pin of exactly half an inch in length fixed on one side of it. This being laid across the mouth of the phial with the pin downwards in the neck, the solution was poured into the phial till it reached the point of the pin. The brass plate and pin being removed, the neck was then filled up with distilled water, with the aid of the little float as formerly. The water-jar, in which the solution-phial stood, was filled up with water also as formerly, so as to cover the phial entirely to the depth of 1 inch. This water-atmosphere amounted to 8750 grs. or about 20 ounces. A glass plate was placed upon the mouth of the water-jar itself to prevent evaporation. Sometimes 80 or 100 diffusion cells were put in action at the same time. The period of diffusion chosen was now always exactly seven days, unless otherwise mentioned.

#### DIFFUSION OF SALTS OF POTASH AND AMMONIA.

Solutions were prepared of the various salts, in a pure state, in certain fixed proportions, namely, 2, 4, 6½ and 10 parts of salt to 100 parts of water by weight. The density of these solutions was observed by the weighing-bottle, at 60°. The solutions were frequently diffused at two different temperatures; one, the temperature of the atmosphere, which was fortunately remarkably constant during most of the experiments to be recorded at present, and the other, a lower temperature, obtained in a close box of large dimensions, containing masses of ice. The results at the artificial temperature were obviously less accurate than those of the natural temperature, but have still considerable value. Three experiments were generally made upon the diffusion of each solution at the higher, with two experiments at the lower temperature. The diffusion-products are expressed in grains.

The mean diffusion of the different solutions containing 2, 4, 6½ and 10 parts of certain salts was as follows:

Diffusion at 64°·2:

	2.	4.	6½.	10.
Carbonate of potash . .	5·45	10·25	16·67	24·69
Sulphate of potash . .	5·52	10·57	17·17	23·62
Sulphate of ammonia . .	5·58	10·51	16·79	22·20

Diffusion at  $37^{\circ}6$  :

	2.	4.	6 $\frac{2}{3}$ .
Carbonate of potash . . .	3.85	7.09	11.25
Sulphate of potash . . .	3.95	7.40	11.66
Sulphate of ammonia . . .	3.76	7.70	10.96

The proportions diffused are sensibly equal, of the different salts, at the higher temperature, with the exception of the largest proportion of salt, 10 per cent, when a certain divergence occurs. This last fact is consistent with the expectation, that the diffusion of salts would prove most highly normal in dilute solutions. Some of the irregularities at the lower temperature are evidently of an accidental kind.

The neutral chromate and acetate of potash were diffused at a temperature ranging from  $63^{\circ}$  to  $65^{\circ}$ , or at a mean temperature of  $64^{\circ}1$ , which almost coincides with the higher temperature of the last experiments.

Diffusion at  $64^{\circ}1$  :

	2.	4.	6 $\frac{2}{3}$ .	10.
Chromate of potash . . .	5.77	11.19	17.60	24.75
Acetate of potash . . .	5.85	10.70	16.48	24.85

The 10 per cent solution of these two salts also agrees with the same solution of carbonate of potash, which was 24.69 grs. Nor do the lower proportions diverge greatly from the preceding group of salts.

Another pair of salts were simultaneously diffused, but with an accidental difference of  $0^{\circ}4$  of temperature.

Mean diffusion at  $64^{\circ}1$  and  $64^{\circ}5$  :

	2.	4.
Bicarbonate of potash . . . .	5.81	11.01
Bichromate of potash . . . .	5.65	11.49

It is singular to find that salts differing so much in constitution and atomic weight as the chromate and bichromate of potash, may be confounded in diffusibility. The diffusion-products of these two salts are, for the 2 per cent solutions, 5.77 and 5.65 grs. and for the 4 per cent solution, 11.19 and 11.49 grs. The bicarbonate of potash also exhibits a considerable analogy to the carbonate, but resembles still more closely the acetate. It is thus obvious that similarity, or equality, of diffusion is not confined to the isomorphous groups of salts.

The nitrates of potash and ammonia have already appeared to be equidiffusive at two different temperatures. They were diffused again in the same proportions as the last salts, at a temperature varying from  $63^{\circ}$  to  $67^{\circ}5$ .

Diffusion at  $65^{\circ}9$  :

	2.	4.	6 $\frac{2}{3}$ .	10.
Nitrate of potash . . .	7.47	13.97	22.37	32.49
Nitrate of ammonia . . .	7.73	14.48	22.74	34.22

Although these salts correspond closely, it is probable that neither the diffusion of these nor the diffusion of any others is absolutely identical. The nitrate of ammonia appears to possess a slight superiority in diffusion over the nitrate of potash, which increases with the large proportions of salt in solution. They are both considerably more diffusible than the seven preceding salts.

A second pair of isomorphous salts were compared, the chlorides of potassium and ammonium.

Diffusion at 66°·2 :

	2.	4.	6½.	10.
Chloride of potassium .	7·70	15·29	24·87	36·93
Chloride of ammonium .	7·81	14·60	24·30	36·53

The quantities diffused of these two chlorides are more closely in proportion to the strength of the original solution, than with any of the preceding salts of potash. Thus the quantities diffused from the 2 and 10 per cent solutions of chloride of potassium are 7·70 and 36·93 grs., which are as 2 to 9·6, or nearly as 2 to 10. Chloride of sodium was observed before to be nearly uniform in this respect; but other salts appear to lose considerably in diffusibility with the higher proportions of salt. It is possibly a consequence of the crystallizing attraction, to which reference was lately made, coming into action in strong solutions and resisting diffusion.

The salts of potash thus appeared to fall into two groups, the members of which have a nearly equal diffusibility, at least from weak solutions, such as 1 or 2 per cent. Of what may be called the sulphate of potash class the diffusion from 1 per cent solutions was as follows :

Diffusion of 1 per cent solutions at 58°·5 :

Carbonate of potash . . . .	2·63	grs.
Sulphate of potash . . . .	2·69	„
Acetate of potash . . . .	2·68	„
Chromate of potash . . . .	2·83	„
Bicarbonate of potash . . . .	2·81	„
Bichromate of potash . . . .	2·88	„

Diffusion of salts of the nitre class at 64°·5 :

	1.	2.	4.
Nitrate of potash . . .	3·72	7·47	13·97
Nitrate of ammonia . .	3·75	7·73	14·48
Chloride of potassium .	3·88	7·70	15·01
Chloride of ammonium .	3·89	7·81	14·41
Chlorate of potash . .	3·66	7·22	13·31
Mean . . . .	3·78	7·58	14·23

What is the relation between these groups ?

The diffusion of 4 per cent solutions of carbonate and nitrate of potash was repeated at a temperature rising gradually from  $63^{\circ}$  to  $65^{\circ}$  during the seven days of the experiment, with a mean of  $64^{\circ} \cdot 1$ . The diffusion-products of the carbonate were 10·31, 10·05 and 10·44 grs. in three cells; mean 10·27 grs. Of the nitrate, 13·98, 13·86 and 13·60 grs.; mean 13·81 grs. There is thus a diffusion in equal times of:

Carbonate of potash . . .	10·27	1
Nitrate of potash . . .	13·81	1·3447

But the numbers so obtained cannot be fairly compared, owing to the diminishing progression in which the diffusion of a salt takes place. Thus when the diffusion of nitrate of potash was interrupted every two days, as in a former experiment with chloride of sodium, the progress of the diffusion for eight days was found to be as follows in a 4 per cent solution, with a mean temperature of  $66^{\circ}$ .

Nitrate of potash :

Diffused in first two days . . . .	4·54 grs.
Diffused in second two days . . . .	4·13 „
Diffused in third two days . . . .	4·06 „
Diffused in fourth two days . . . .	3·18 „

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15·91

The absence of uniformity in this progression is no doubt chiefly due to the want of geometrical regularity in the form of the neck and shoulder of the solution-phial. A plain cylinder, as the solution cell, might give a more uniform progression, but would increase greatly the difficulties of manipulation.

The diffusion of carbonate of potash will no doubt follow a diminishing progression also; but there is this difference, that the latter salt will not advance so far in its progression, owing to its smaller diffusibility, in the seven days of the experiment, as the more diffusible nitrate does. The diffusion of the carbonate will thus be given in excess, and as it is the smaller diffusion, the difference of the diffusion of the two salts will not be fully brought out.

The only way in which the comparison of the two salts can be made with perfect fairness, is to allow the diffusion of the slower salt to proceed for a longer time, till in fact the quantity diffused is the same for this as for the other salt, and the same point in the progression has therefore been attained in both; and to note required. The problem takes the form of determining the times of equal diffusion of the two salts. This procedure is the more necessary from the inapplicability of calculation to the diffusion progression.

Further, allowing the Times of Equal Diffusion to be found, it is

not to be expected that they will present a simple numerical relation. Recurring to the analogy of gaseous diffusion, the times in which equal volumes or equal weights of two gases diffuse are as the square roots of the densities of the gases. The times, for instance, in which equal quantities of oxygen and hydrogen escape out of a vessel into the air, in similar circumstances, are as 4 to 1, the densities of these two gases being as 16 to 1. Or, the times of equal diffusion of oxygen and protocarburetted hydrogen are as 1.4142 to 1, that is as the square root of 2 to the square root of 1, the densities of these gases being 16 and 8, which are as 2 to 1. The densities are the squares of the equal-diffusion times. It is not therefore the times themselves of equal diffusion of two salts, but the squares of those times which are likely to exhibit a simple numerical relation.

While the 4 per cent solution of nitrate of potash was diffused as usual for seven days, the corresponding solution of carbonate of potash was now allowed to diffuse for 9.90 days; times which are as 1 to 1.4142.

The results were as follows: diffused of—

Nitrate of potash at 64 <sup>0</sup> .1, in seven days, 13.81 grs.	. . . 100
Carbonate of potash at 64 <sup>0</sup> .3 in 9.9 days, 13.92 „	. . . 100.8

The three experiments on the nitrate of potash, of which 13.81 grs. is the mean, were 13.98, 13.86 and 13.60 grs. as already detailed. The three experiments on the carbonate were 14.00, 13.97 and 13.78 grs. The difference in the means of the two salts is only 0.11 gr.

The explanation of such a relation suggested by gaseous diffusion is that the molecules of the two salts, as they exist in solution, have different densities, that of nitrate of potash being 1, and that of carbonate of potash 2. We are thus led to ascribe densities to the solution-molecules of the salts, conceived on the analogy of vapour-densities. The two salts in question are related exactly like protocarburetted hydrogen gas, of density 1, to oxygen gas of density 2. The parallel would be completed by supposing that the single volume of oxygen to be diffused was previously mixed with 100 volumes of air (or any other diluting gas), while the 2 volumes of protocarburetted hydrogen were also diluted with 100 volumes of air; the diluting air here representing the water in which the salts to be diffused are dissolved in the solution-*phial*. The time in which a certain quantity of protocarburetted hydrogen would come out from a vessel containing 1 per cent of that gas being 1 (the square root of density 1), the time in which an equal quantity of oxygen would diffuse out from a similar vessel containing 1 per cent also, would be 1.4142 (the square root of density 2).

The diffusion was repeated of 2 per cent solutions of the nitrate and carbonate of potash at a lower temperature by about 10<sup>0</sup>.

The mean results were :

Nitrate of potash in seven days, 12·22 grs. in two cells . 100  
Carbonate of potash in 9·9 days, 12·40 „ „ . 101·47

Again at a still lower temperature, the times being still as 1 to 1·4142.

The results were :

1 per cent solution of nitrate of potash in  
nine days at 39°·7 . . . . . 6·83 grs. . 100  
" " " " sulphate of potash in  
12·728 days at 39°·7 . . . . . 7·04 „ . 103·07

With 2 per cent solutions at the same temperature :

Nitrate of potash, 6·83 grs. . . . . 100  
Sulphate of potash, 6·82 „ . . . . 99·85

The existence of the relation in question was also severely tested in another manner. Preserving the ratio in the times of diffusion for the two salts, the actual times were varied in duration, in three series of experiments, as 1, 2 and 3. The experiments were made in a vault, with a uniformity of temperature favourable to accuracy of observation. Eight cells of the 1 per cent solution of each salt were always diffused at the same time.

3·5 and 49·5 days	{ Nitrate of potash, at 47°·2, 3·50 grs.	100
	{ Sulphate of potash, at 47°·3, 3·50 grs.	100
7 and 9·9 days	{ Nitrate of potash, at 48°·6, 6·04 grs.	100
	{ Sulphate of potash, at 49°·1, 6·20 grs.	102·65
	{ Chromate of potash, at 49°·1, 6·29 grs.	104·14
10·5 and 14·85 days	{ Nitrate of potash, at 48°·8, 8·74 grs.	100
	{ Sulphate of potash, at 48°·6, 8·79 grs.	100·57

The concurring evidence of these three series of experiments is strongly in favour of the assumed relation of 1 to 1·4142, between the times of equal diffusion for the nitrate and sulphate of potash, and consequently of the times for the two classes of potash-salts, of which the salts named appear to be types. The same experiments are also valuable as proving the similarity of the progression of diffusion, in two salts of unequal diffusibility.

*Hydrate of potash.*—Of pure fused hydrate of potash, a 1 per cent solution was diffused from four cells for 4·95 days at a mean temperature of 53°·7, against a 1 per cent solution of nitrate of potash in six cells, for seven days, at a mean temperature 0°·1 lower, or of 53°·6. The hydrate of potash which diffused, was calculated from the chloride of potassium which it gave, when neutralized by hydrochloric acid. Hydrate of potash diffused in two cells 5·97 and 6·28 grs.; mean 6·12 grs., or 3·06 grs. for a single cell.



Nitrate of potash diffused in two cells 6·22, 6·54 and 5·93 grs.; mean 6·23 grs., or 3·11 grs. for a single cell. The diffusion of nitrate of potash being 100, that of the hydrate of potash is 98·2, numbers which are sufficiently in accordance. But the times were as 1 to 1·4142, and their squares as 1 to 2. So far then as one series of experiments on hydrate of potash entitles us to conclude, we appear to have for the salts of potash a close approximation to the following simple series of times of equal diffusion, with the squares of these times.

	Times.	Squares of times.
Hydrate of potash . . .	1	1
Nitrate of potash . . .	1·4142	2
Sulphate of potash . . .	2	4

The diffusion of hydrate of potash, at 39°·7, with reference to corresponding solutions of nitrate of potash, for the selected times, was as follows:

Nitrate of potash, 1 and 2 per cent solutions . . .	100
Hydrate of potash, 1 per cent solution . . . . .	101·3
Hydrate of potash, 2 per cent solution . . . . .	99·4

These experiments at the low temperature concur, therefore, with those made at the higher temperature, in proving that the times of equal diffusion of the two substances have been properly chosen.

*Diffusion of salts of soda.*—The only salts of soda which have yet been diffused in a sufficient variety of circumstances are the carbonate and sulphate. These salts appear to be equidiffusive, but to diverge notwithstanding more widely in solutions of the higher proportions of salt than the corresponding potash-salts. It is a question whether this increased divergence is not due to the less solubility of the soda-salts, and the nearer approach consequently to their points of saturation in the stronger solutions.

The mean results at 64° were as follows:

	2.	4.	6½.	10.
Carbonate of soda . . .	4·14	7·78	12·22	16·88
Sulphate of soda . . .	4·31	8·17	13·50	19·14

#### DIFFUSION OF 1 PER CENT SOLUTIONS AT 64°·9

Carbonate of soda, 2·32 grs. . . . .	100
Sulphate of soda, 2·38 „ . . . . .	102·58

The diffusion of the carbonate of soda was further compared with the nitrate of the same base, to find whether their times of equal diffusion are related like those of the corresponding potash-salts.

1 per cent solution of nitrate of soda, in 7 days, at 66°·9, in four cells, 11·73 grs. . . . .	100
1 per cent solution of carbonate of soda, in 9·9 days, at 66°·9, 11·62 grs. . . . .	99·06
2 per cent solution of nitrate of soda, in 7 days, at 54°·3, 10·10 grs. . . . .	100
2 per cent solution of carbonate of soda, in 9·9 days, 9·95 grs. . . . .	98·51

It appears probable therefore that the times of equal diffusion of the nitrate and carbonate of soda are related like those of the nitrate and carbonate of potash, that is, as 1 to 1·4142.

In conclusion, the results of most interest may be summed up, which this inquiry respecting liquid diffusion has hitherto furnished.

1. The method may be placed first of observing liquid diffusion. This method, although simple, appears to admit of sufficient exactness. It enables us to make a new class of observations which can be expressed in numbers, and of which a vast variety of substances may be the object; in fact everything soluble. Diffusion is also a property of a fundamental character, upon which other properties depend, like the volatility of substances; while the number of substances which are soluble, and therefore diffusible, appears to be greater than the number of volatile bodies.

2. The novel scale of solution-densities possessed by the molecules of salts when liquid and in solution, which are suggested by the different diffusibilities of salts, and to which alone, guided by the analogy of gaseous diffusion, we can refer these diffusibilities. Liquid diffusion thus supplies the densities of a new kind of molecules, but nothing more respecting them.

The fact that the relations in diffusion of different substances refer to equal weights of those substances, and not to their atomic weights or equivalents, is one which reaches to the very basis of molecular chemistry. The relation most frequently possessed is that of equality, the relation of all others most easily observed. In liquid diffusion we appear to deal no longer with chemical equivalents or the Daltonian atoms, but with masses even more simply related to each other in weight. Founding still upon the chemical atoms, we may suppose that they can group together in such numbers as to form new and larger molecules of equal weight for different substances, or if not of equal weight, of weights which appear to have a simple relation to each other. It is this new class of molecules which appear to play a part in solubility and liquid diffusion, and not the atoms of chemical combination.

3. The formation of classes of equidiffusive substances. These classes are evidently often more comprehensive than the isomorphous groups.

4. The separation of the whole salts (apparently) of potash and of soda into two divisions, the sulphate and nitrate groups, which must have a chemical significancy. The same division of the salts in question has been made by M. Gerhardt, on the ground that the nitrate class is monobasic and the sulphate class bibasic, and is further supported by the state of condensation of the vapours of acids belonging to the different groups, the equivalent of hydrochloric acid giving 4 and that of sulphate of water 2 volumes of vapour, a relation quite analogous to that observed in the "solution-densities."

5. The application of liquid diffusion to the separation of mixed salts, in natural and in artificial operations.

6. The application of liquid diffusion to produce chemical decompositions.

7. The assistance which a knowledge of liquid diffusion will afford in the investigation of endosmose. When the diffusibility of the salts contained in a liquid is known, the compound effect presented in an endosmotic experiment may be analysed, and the true share of the membrane in the result be ascertained.

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**Researches regarding the Molecular Constitution of the Volatile Organic Bases.**

**By Dr. A. W. Hofmann, F.C.S.\***

Among the various classes of organic substances, there is perhaps none of which, from an early period, chemists have so constantly endeavoured to attain a general conception as the group of compounds which have received the name of organic bases, all—and they are now very numerous—being capable of combining, like the metallic oxides, with acids, and being derived either from vital processes in animals or plants, or from a variety of artificial reactions conducted in the laboratory.

The remarkable analogy between all these substances and ammonia, which in its turn imitates, as it were, in its chemical deportment the mineral oxides, naturally attracted the notice of chemists soon after Sertürner's discovery of the first of these alkaloids in the beginning of this century. Nor have they ever since been classified separately from ammonia; philosophers have only differed as to the mode of their relation with the typical compound.

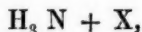
Of the theories which have been enunciated respecting the constitution of the organic bases, there are two of chief importance, which may be designated as the ammonia- and the amidogen-theory, the former having been first proposed by Berzelius,† while the latter

\* Phil. Trans. 1850, I, 93.

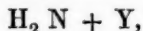
† Traité de Chimie, VI, 2.

we owe to Liebig.\* According to the former of the two chemists, the ammonia would pre-exist in the organic bases; these bodies would be conjugated compounds of ammonia with various adjuncts, containing either carbon and hydrogen, or these elements together with nitrogen, oxygen, and even sulphur, compounds in which the original character of the ammonia has only been slightly modified by the accession of the adjunct. This view is chiefly supported by the mode and the proportions in which these alkaloids combine with acids, and by the fact, that various organic substances, by directly uniting with ammonia, give rise to the formation of basic compounds which are perfectly analogous to the alkaloids occurring in the economy of nature. According to Liebig's opinion, ammonia would no longer exist in the organic bases. At the time when Liebig† wrote upon this subject, the attention of chemists was much engaged with the study of the amides, the prototype of which, oxamide, had then been discovered by Dumas. These substances, all strictly neutral, originate from ammonia by the loss of 1 equivalent of hydrogen, which is abstracted by the oxygen or chlorine of certain electro-negative bodies (as in the formation of oxamide and benzamide), a hypothetical substance, amidogen,  $H_2 N$ , remaining in combination with the oxide or chloride, deprived of 1 equiv. of oxygen or chlorine. Liebig thought that the formation of the organic bases might take place in a similar manner, namely, by a reduction of ammonia to the state of amidogen, by the action of electro-positive organic oxides.

Each of these theories being expressed in a simple formula, the organic bases, according to Berzelius, would be represented by the terms



while Liebig's view would characterize them as



X denoting generally an organic compound containing carbon, hydrogen, and possibly nitrogen, oxygen and sulphur; while Y expresses an organic oxide, chloride, &c., *minus* 1 equiv. of oxygen, chlorine, &c.

Objections have been raised against either theory, and the opinions of chemists have remained divided. Liebig has not returned any more to the subject, but Berzelius took frequent occasion, both in his "Annual Report," and in the several editions of his "Traité," to defend his notion by the skilful interpretation of every new fact which was elaborated by the progress of the science. The weight of

\* Handwörterbuch der Chemie von Liebig, Wöhler, und Poggendorff, Bd. I, 699. Artikel, *Organische Basen*.

† Loc. cit. 235.

his authority has not been without influence, for it cannot be denied that Berzelius's view has become more and more generally accepted, especially since a series of comparative researches, conducted of late upon the derivatives of the salts of ammonia and of organic bases, appeared to give fresh support to this theory. These experiments pointed out that the elimination of hydrogen from organic bases and ammonia is by no means confined to 1 equivalent; oxalate of ammonia, which, by the loss of 2 equivs. of water is converted into oxamide, when deprived of the whole of its hydrogen, in the form of water, becomes cyanogen (oxalonitrile); an analogous change occurs with the acid salts of ammonia, resulting in the formation of two classes of compounds, differing, the one by 2, the other by 4 equivalents of water, from the original salt.

The representation of several of these groups in analogous derivatives from the salts of organic bases, especially from the salts of aniline, could not but strengthen the belief that ammonia actually pre-exists in the organic alkaloids. Incidentally to some researches communicated to the Chemical Society of London,\* I gave a synopsis of all the facts supporting the view of Berzelius.

The prosecution, however, of this inquiry has elicited many points, which are scarcely reconcilable with this theory. In another paper† I endeavoured to show that the force of the argument in favour of this view, derived from the considerations just stated, is greatly neutralized, on the completion of the comparison between the two series, by the failure of the analogy, just at the point where its occurrence would have been most decisive. Now this very failure is not only in perfect harmony with, but would be required by, the theory of amidogen-bases.

Yet stronger grounds for the acceptance of the latter view have been afforded by a splendid investigation of M. Wurtz‡ on the compounds of ethers with cyanic acid, which have actually realized a series of substances, anticipated in a most remarkable manner by Liebig on the theoretical ground of his conception of the nature of these compounds. Instances of such anticipation of discovery are so rare, that I may be allowed to quote the words in which Liebig predicted nearly ten years ago the discovery of M. Wurtz:—"If," said Liebig,§ in continuing the development of his ideas respecting the constitution of the organic bases, "we were enabled to replace by amidogen the oxygen in the oxides of methyl and ethyl, in the oxides of two basic radicals, we should without the slightest doubt

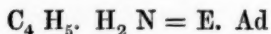
\* Researches on the Volatile Organic Bases, III. Action of Chloride, Bromide and Iodide of Cyanogen upon Aniline; Chem. Soc. Qu. J. I, 285.

† Chem. Soc. Qu. J. II, 331.

‡ Compt. Rend. XXVIII, 223

§ Loc. cit. 235.

obtain a series of compounds exhibiting a deportment similar in every respect to that of ammonia. Expressed in symbols, a compound of the formula



would be endowed with basic properties."

Now these compounds, imagined in 1840 by Liebig in illustration of his views, have sprung into existence in 1849, with all the properties assigned to them by that chemist. At the beginning of the present year, M. Wurtz, in investigating the cyanates of ethyl, methyl and amyl, arrived at the unexpected result, that these compounds, when decomposed by potassa, undergo a change analogous to that of cyanic acid. This acid, when treated with potassa, yielding carbonic acid and ammonia, the corresponding ethers were split into carbonic acid and compound ammonias of the exact formula indicated in Liebig's suggestion.

It would be difficult to imagine a more brilliant triumph for any theoretical speculation; I have, however, no doubt that even the illustrious propounder of this view is at present far from believing that all the organic bases are amidogen-compounds. The progress of our knowledge has changed the form of this view, without shaking its foundation. A good theory is more than a *temporary* expression of the state of science, collecting under a general view the facts acquired up to the moment of its birth. It will not, like ephemeral hypothesis, vanish before the light of succeeding discoveries, but expanding with the growth of science, it will still correctly represent the known facts, though of necessity modified into a more general expression.

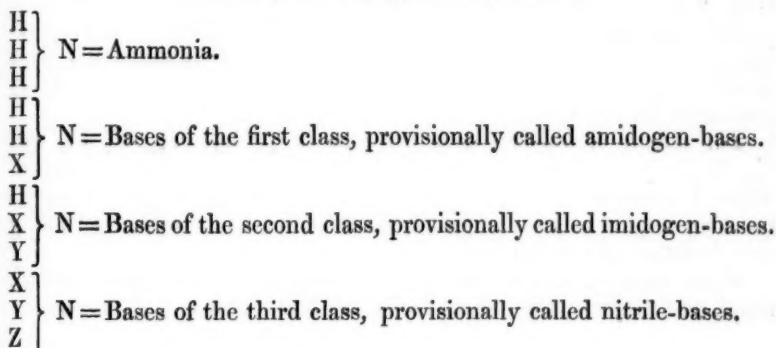
Such a theory then was that of Liebig. Resting as it did, upon the facts observed in the formation of the neutral amides, it was, as originally framed, an expression of the knowledge we then possessed. Subsequent researches showed that it was not only the 1 equivalent of hydrogen (the abstraction and replacement of which had led us to amidogen and the amides) that could be removed from the ammonia, but that similarly 2 equivalents, and even the whole of the hydrogen, could be withdrawn from their position in this base and substituted by other atoms, as in the imides and nitriles.

If then we give to Liebig's view the extension of which it naturally admits, and which is demanded by the onward steps of science, we arrive at a more general conception of the nature of the organic bases; amidogen and the amides now presenting themselves to us only as particular instances of the permutations possible among the elements of the primary type ammonia. It seemed but logical to look among the bases for analogues too of the imidogen-compounds and the nitriles. In other words, it appeared desirable to inquire

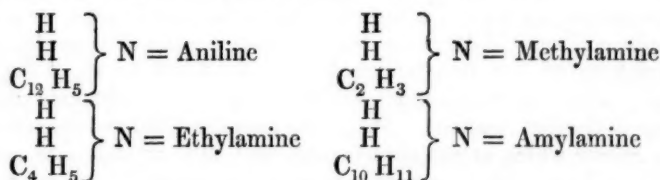


whether the several equivalents of hydrogen in ammonia could not be replaced, not only by atoms neutralizing the basic properties of the original system, but also by elements or groups of elements, not affecting, or but slightly modifying the alkaline character of the primary compound. Were this possible, we should arrive at the formation of three classes of organic bases, derived from ammonia by the replacement respectively of 1, 2 or 3 equivalents of hydrogen.

Expressed in formulæ, these compounds would be :



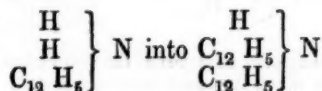
The bases belonging to the first class are pretty numerously represented. Aniline, methylamine, ethylamine, amylamine, when considered as amidogen-compounds, belong to this group.



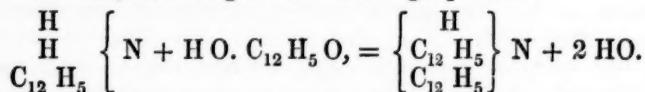
Bases of the second and third of the above classes had not been hitherto obtained, although it is not improbable that many of the alkaloids, whose constitution is at present perfectly unknown, may be found on a closer investigation to be members of these latter groups.

#### ACTION OF PHENYL-ALCOHOL ON ANILINE.

My endeavours to introduce into aniline a second equivalent of phenyl, in order to convert



have been unsuccessful up to the present moment. I had hoped that this conversion might be effected by the action of phenyl-alcohol on aniline, according to the following equation :



Phenyl-alcohol, however, has neither at the common nor at a high temperature—the mixture was exposed for several days in a sealed tube to 250° in an oil-bath—any action upon aniline.

This experiment, when repeated for a longer period, might possibly give a more satisfactory result. It is known that ammonia, by a similar treatment with phenyl-alcohol, is likewise only very slowly converted into aniline.

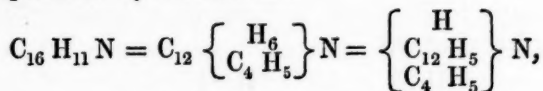
The action of chloride and bromide of phenyl  $\text{C}_{12} \text{H}_5 \text{Cl}$ , and  $\text{C}_{12} \text{H}_5 \text{Br}$  upon aniline promised a better result ; but the difficulties which I encountered in preparing these compounds, which are as yet but very imperfectly investigated, deterred me from further pursuing this direction of the inquiry.

Much more successful were my endeavours to substitute methyl, ethyl, and amyl for the remainder of the basic hydrogen in aniline.

#### ACTION OF BROMIDE OF ETHYL UPON ANILINE.

On adding dry bromide of ethyl to aniline, no change takes place in the cold, but on gently heating the mixture in an apparatus which will allow the volatilized bromide to return to the aniline, a lively reaction ensues. The liquid remains for some time in a state of ebullition, and solidifies on cooling into a mass of crystals. If a cold mixture of the two bodies be left for a few hours, it deposits crystals, which are much more definite than those obtained on the cooling of the hot solution. In either case the fluid assumes a deep amber colour which approaches brown, and the crystals are usually slightly yellow. These crystals vary in composition according to the proportions in which the two bodies have been mixed. If a very large excess of aniline has been used, they are of a prismatic character, and consist of pure hydrobromate of aniline.

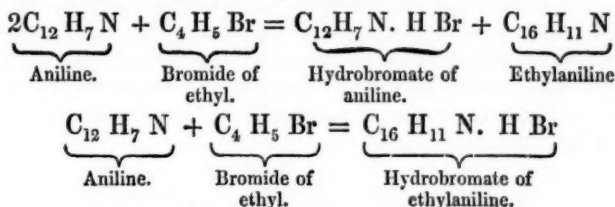
On the other hand, if the bromide of ethyl predominates to a considerable extent, the crystals are flat, four-sided tables, sometimes of considerable size. Several analyses, the details of which will be found below, showed that they were the hydrobromate of a new base,\* represented by the formula :



\* Frequently, as may be imagined, mixtures of the two hydrobromates are deposited according to the proportion in which the constituents are mixed.

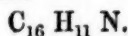
*i. e.* of aniline in which 1 equiv. of hydrogen is replaced by 1 equiv. of ethyl, or ammonia in which 2 equivs. of hydrogen are replaced, the one by phenyl, the other by ethyl. The same base is contained in the free state, either alone or mixed with aniline in the mother-liquor of the crystals of hydrobromate of aniline; while the mother-liquor of the hydrobromate of the new base, especially if a large excess of the bromide has been employed, and after some days' standing, consists of nearly perfectly pure bromide of ethyl, only a small quantity of the hydrobromate in question being kept in solution.

The formation of the new basic compound, for which I propose the name *Ethylaniline* or *Ethylophenylamine*, takes place by the removal, from aniline, of 1 equiv. of hydrogen, in the form of hydrobromic acid, for which an equivalent of ethyl is substituted, the compound thus produced uniting with the hydrobromic acid. Hence the action of bromide of ethyl upon aniline may be represented by the following two simple equations:



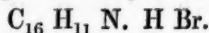
*Ethylaniline (Ethylophenylamine).*—This base may be readily obtained in a state of purity by decomposing the solution of the hydrobromate with a concentrated solution of potassa. A brown basic oil rises at once to the top of the liquid; it is separated by means of a pipette or a tap-funnel, and subjected to rectification, after having been freed from water by standing over solid potassa. Thus a colourless transparent oil is obtained, which rapidly turns brown on exposure to air and light, and has a very high refractive power. It has all the properties of the oily bases in general. From aniline it is distinguished by a slight difference in the odour, perhaps imperceptible to an inexperienced nose, by a higher boiling-point, and a lower specific gravity. *Ethylaniline* boils (from platinum) constantly at  $204^{\circ}$ , the boiling-point of aniline being  $182^{\circ}$ ; the specific gravity of this base is 0.954 at  $18^{\circ}$ , that of aniline being 1.020 at  $16^{\circ}$ . *Ethylaniline* does not exhibit the violet coloration with chloride of lime which characterizes aniline. Its acid solutions impart a yellow colour to fir-wood and the pith of elder-tree, although less intensely than those of aniline. By dry chromic acid the base is inflamed like aniline.

Analysis led to the formula:

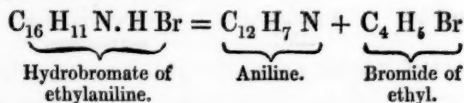


The salts of ethylaniline are remarkable for their solubility, especially in water. They are not easily obtained in well-defined crystals from an aqueous solution. From alcohol, in which they are somewhat less soluble than in water, several salts may be readily crystallized. Both the hydrochlorate and oxalate are obtained only on evaporating their solutions nearly to dryness, when the salts separate in the form of radiated masses; the sulphate and nitrate have not as yet been obtained in the solid form.

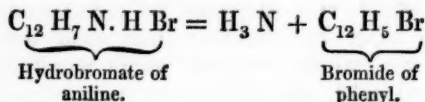
*Hydrobromate of Ethylaniline.*—The hydrobromate is extremely soluble in water, but crystallizes on spontaneous evaporation of its alcoholic solution in splendid regularly formed tables, of considerable size and perfect beauty. I intend to give the measurement of these crystals in a future communication. The composition of this salt, dried at 100°, is represented by the formula,



The hydrobromate of ethylaniline when gently heated sublimes, like the corresponding aniline-salt, in splendid needles, but when subjected to the action of a rapidly increasing heat it undergoes a very remarkable decomposition, being redecomposed into aniline and bromide of ethyl. On addition of hydrochloric acid to the distillate, the aniline dissolves, while the bromide of ethyl collects as a heavy oil at the bottom of the vessel.



I have in vain tried to split hydrobromate of aniline according to the equation

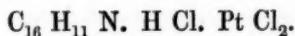


This salt sublimes, even when suddenly heated, without any decomposition.

*Platinum-salt of Ethylaniline.*—I have controlled the formula of ethylaniline, moreover, by the analysis of the platinum double salt of this substance. This salt is likewise very soluble, and may by this property be distinguished from the corresponding aniline-salt; on addition of a concentrated solution of bichloride of platinum to a concentrated solution of this hydrochlorate, a deep orange-red oil is deposited, which solidifies, sometimes only after half a day, with crystalline texture. If a moderately concentrated solution be employed, the salt crystallizes in the course of a few hours in magnificent yellow needles, often an inch in length. On account of its great solubility in water and alcohol, it has to be washed with a

mixture of alcohol and ether, in which the latter predominates. It may be dried at 100° without decomposition.

Formula :



Tetrachloride of gold and protochloride of mercury yield, with solutions of ethylaniline, yellow oily precipitates, which are very readily decomposed.

Of the products of decomposition of ethylaniline, I know as yet almost nothing, although they will not be deficient in interest in a theoretical point of view.

The action of bromine gives rise to the formation of two compounds, both crystalline, one basic, the other indifferent and corresponding probably to tribromaniline. Neither of these substances has yet been analysed.

On passing cyanogen into an alcoholic solution of ethylaniline, short yellow prisms are deposited after some time, which are evidently cyanethylaniline, Cy.  $\text{C}_{16} \text{H}_{11} \text{N}$ , corresponding to cyaniline and cyanocumidine.\* This new cyanogen-base dissolves in dilute sulphuric acid, and is thrown down from this solution by ammonia in form of a floury precipitate. The hydrochlorate, like the corresponding cyaniline-salt, is very insoluble in hydrochloric acid. It may be obtained in fine crystals on addition of hydrochloric acid to a solution of the base in dilute sulphuric acid. Cyanethylaniline, like cyaniline, forms a very soluble platinum-salt.

I have made also some qualitative experiments respecting the deportment of ethylaniline with chloride of cyanogen. This gas is rapidly absorbed, much heat being evolved. On cooling, the mass solidifies into a resinous mixture of a hydrochlorate and a neutral oil, which separates on addition of water. The base separated from the hydrochlorate is an oil, and volatile; while melaniline, produced in the corresponding reaction of chloride of cyanogen with aniline, is solid and non-volatile.

Bisulphide of carbon gives rise to a gradual evolution of hydro-sulphuric acid, no crystals being deposited from the mixture.

Phosgene gas acts powerfully on ethylaniline, a liquid compound being formed, together with hydrochlorate of ethylaniline. No analysis having as yet been performed of these compounds, I refrain from entering into any further details.

#### ACTION OF BROMIDE OF ETHYL UPON ETHYLANILINE.

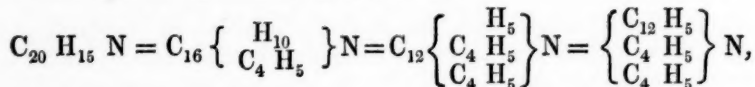
The phenomena attending the action of bromide of ethyl upon ethylaniline resemble those which are observed in the corresponding treatment of aniline. The reaction, however, is less powerful, another

\* Chem. Soc. Qu. J. I, 159.

equivalent of hydrogen in aniline being less easily eliminated or replaced. Four or five days elapse before the separation of crystals commences at common temperatures. The formation, however, is considerably accelerated on application of heat.

The experience obtained in the preparation of ethylaniline suggested at once the use of a very large excess of bromide of ethyl, by which the formation of one compound only was secured. The mixture assumed a light-yellow colour, turned gradually brown, and deposited after five days four-sided tables of considerable size and remarkable beauty. The mother-liquor was coloured bromide of ethyl, leaving, when distilled off, a small quantity of the same crystalline compound.

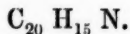
The substance in question was the pure hydrobromate of a new base, which is represented by the formula :



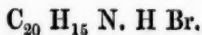
*i. e.* of ethylaniline in which 1 equiv. of hydrogen is replaced by ethyl, or aniline in which 2 equivs. of the same radical are substituted for a corresponding number of hydrogen-equivalents, or lastly ammonia, in which the 3 equivalents of hydrogen are replaced, the one by phenyl, the two others each by ethyl.

The formation of this new substance, for which I propose the name diethylaniline or diethylophenylamine, requires no further illustration: it is absolutely analogous to the production of ethylaniline.

*Diethylaniline (Diethylophenylamine).*—The preparation of this compound in a state of purity resembles that of the preceding base, whose physical properties have been only slightly modified by the introduction of the second equivalent of ethyl. The specific gravity was found to be 0.939 at 18°, showing a slight decrease when compared with that of ethylaniline (0.954). The boiling-point, however, was raised nearly 10 degrees; diethylaniline boils quite constantly at 213°.5. Diethylaniline is moreover distinguished from ethylaniline by remaining perfectly bright and colourless when exposed to the air. Like ethylaniline, it still imparts a yellow colour to fir-wood; but, like the former, fails to affect a solution of hypochlorite of lime. Composition :



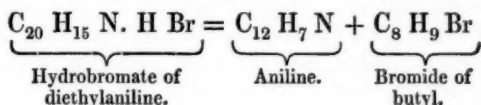
*Hydrobromate of Diethylaniline.*—I have mentioned this salt when speaking of the formation of the second base. It is extremely soluble, and resembles in every respect the corresponding ethylaniline-compound. Composition :





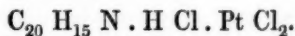
The hydrobromate of diethylaniline, when gently heated, fuses and sublims like the corresponding aniline- and ethylaniline-salts. When rapidly heated, it is entirely converted into a colourless oil, which distils over. This oil contains equal equivalents of bromide of ethyl and ethylaniline. By this distillation, we obtain indeed the very constituents from which the hydrobromate was originally prepared, and which would of course reconvert themselves into hydrobromate of diethylaniline. Only a trifling amount of undecomposed hydrobromate covers, after the distillation is finished, the sides of the retort in the form of a radiated coating.

The peculiar deportment then of the hydrobromates of the ethyl-bases, and probably of all their salts, allows us to remove the several equivalents of ethyl one after the other from our fabric in the same manner as we had inserted them. When first I became acquainted with diethylated aniline, having then already observed the deportment of the salts of ethylaniline, which under the influence of heat are reconverted into aniline, I indulged for a moment in the pardonable illusion, that the salt of diethylaniline would exhibit the metamorphosis :



a mode of reaction which would have afforded a passage from the ethyl- into the butyl-series. This step, however, is reserved for a more fortunate experimenter.

*Platinum-salt of Diethylaniline.*—This salt resembles the corresponding compound of ethylaniline. On addition of a concentrated solution of bichloride of platinum to the hydrochlorate, it is precipitated in the form of a deep orange-coloured oil, which rapidly solidifies into a hard crystalline mass. If the solutions are mixed in a dilute state, the salt is separated after some time in cross-like yellow crystals. It is not nearly so soluble in water and alcohol as the ethylaniline-salt. Formula :



I have not examined any other of the salts of diethylaniline: their deportment resembles in every respect that of the ethylaniline-salts.

#### ACTION OF BROMIDE OF ETHYL ON DIETHYLANILINE.

If we assume that the series of bases, aniline, ethylaniline, and diethylaniline, arise from the gradual elimination of the 3 equivalents of hydrogen in ammonia, and their substitution by 1 equivalent of phenyl and 2 equivalents of ethyl, it is difficult to imagine that bromide of ethyl should have any further action on diethylaniline.

line, this compound ammonia containing, according to this view, no longer any replaceable hydrogen. This conclusion appears to be supported by a series of experiments performed for this purpose; still the results obtained have elicited some points which require further elucidation.

In aniline, ethylaniline and diethylaniline, then, we have three bases, which may be considered as derived from ammonia by the elimination and replacement of its three hydrogen-equivalents. The successive formations of ethylaniline and diethylaniline from aniline have been detailed in the preceding paragraphs; the passage of ammonia into aniline, when exposed to the action of a phenyl-compound, has been proved at an earlier period by some experiments, made jointly by M. Laurent and myself, upon the action, at a high temperature, of hydrated oxide of phenyl on ammonia. In this reaction a small but unequivocal quantity of aniline is formed.

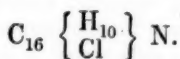
The formation of aniline, ethylaniline and diethylaniline, appeared to have established in a sufficiently satisfactory manner, the point of theory which is here in question; still I thought desirable the acquisition of additional facts in support of the position to which this inquiry has conducted me. Thus I have been led to study the action of bromide of ethyl upon several of the derivatives of aniline, and to try whether other alcohol-radicals, such as methyl and amyl, would have a similar action; lastly, in order to complete the investigation, I was obliged to leave the amidogen-bases altogether, in order to submit the typical ammonia itself to examination.

Among the bases derived from aniline, there is a class whose deportment with bromide of ethyl appeared to be more particularly worthy of a careful investigation. This is the group of compounds produced from aniline by substitution, and embracing chloraniline, dichloraniline and trichloraniline, the corresponding bromanilines, iodaniline and nitraniline. The question arose in what manner will these substances, in which the original aniline has lost already a certain quantity of its hydrogen, comport themselves under the influence of bromide of ethyl? The answer afforded by experiment was unequivocal, and in perfect accordance with the result anticipated by theory, although it may here at once be stated, that the difficulty of obtaining the compounds in question in sufficient quantity has prevented me from pursuing this part of the investigation as far as I could have wished.

#### ACTION OF BROMIDE OF ETHYL UPON CHLORANILINE.

A solution of chloraniline in dry bromide of ethyl exhibits no apparent change even after several days' exposure to the temperature of boiling water. On adding, however, water and distilling off the excess of bromide of ethyl, it was found that the chloraniline had been converted into a hydrobromate, which was held in solution,

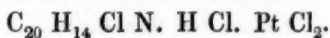
scarcely a trace of uncombined base being left. Addition of potassa to the solution of the hydrobromate separated at once a yellow oily base, of a very characteristic aniseed-odour, differing from chloraniline in many respects. It remained liquid even at the temperature of a cold winter day, while chloraniline is distinguished by the facility with which it crystallizes. Its salts are much more soluble than the corresponding chloraniline-salts: I have only seen the sulphate and oxalate in a crystallized state. This liquid base is evidently ethylochloraniline:



I am sorry that I have not been able to verify this formula by direct analysis. The amount of substance at my disposal precluded the idea of submitting it to the processes of purification necessary before combustion. I had hoped to fix its composition by the determination of the platinum in the platinum-salt. Unfortunately this salt separated in the form of a yellow oil, which could not by any means be made to crystallize. Obligated to desist from direct analysis, I endeavoured to gain the requisite data by another mode of proceeding.

#### ACTION OF BROMIDE OF ETHYL UPON ETHYLOCHLORANILINE.

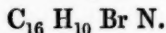
Recollecting that in almost all the instances which I have examined, the tendency exhibited by the various bases of producing readily crystallizable platinum-salts increased with the degree of their ethylation, I subjected the whole amount of the still hypothetical ethylochloraniline, after having dried it by a current of hot air, to the action of a considerable excess of bromide of ethyl. After two days' exposure to 100°, the mixture was found to contain a hydrobromate in solution, not a trace of free base being left. There was no doubt that a second equivalent of ethyl had been assimilated. On decomposing the hydrobromate with potassa, an oil separated, resembling, in its appearance and also in its odour, the preceding compound. An attempt to purify the ethylochloraniline from the potassa by distillation with water having failed, on account of the high boiling-point of this substance, the purification of the diethylochloraniline, for as such the new compound was to be considered, was at once effected with ether. The ethereal solution of the oil was carefully washed with water to remove adhering potassa, and evaporated: the yellow oil remaining after this treatment was dissolved in hydrochloric acid, and the solution mixed with bichloride of platinum. Immediately a splendid orange-yellow crystalline precipitate was separated, which after washing with water was fit for analysis. This salt fused at 100°. Formula:



This result shows that chloraniline, when subjected to the action of bromide of ethyl, exhibits absolutely the same deportment as aniline itself, two equivalents of ethyl being consecutively introduced which give rise to the formation of two new terms, which demand the names ethylochloraniline (ethylochlorophenylamine) and diethylochloraniline (diethylochlorophenylamine).

#### ACTION OF BROMIDE OF ETHYL UPON BROMANILINE.

The absolute analogy existing between chloraniline and bromaniline, to which I have alluded in a former paper,\* is maintained also in the deportment of these two substances towards bromide of ethyl. Bromaniline is rapidly converted into hydrobromate of ethylobromaniline, which could not, except by analysis, be distinguished from the corresponding chlorine-base. The platinum-salt being likewise a viscid oil, I have omitted to analyse it. There is however no doubt about the existence of an ethylobromaniline,



I have not attempted to ethylate this compound any further.

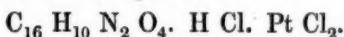
#### ACTION OF BROMIDE OF ETHYL UPON NITRANILINE.

*Ethylonitraniline (Ethylonitrophenylamine).*—Nitraneline readily dissolves in bromide of ethyl. The solution soon deposits, even at the common temperature, pale-yellow crystals of considerable size. At the boiling temperature of water the conversion is rapidly accomplished. On addition of an alkali to the hydrobromate, the ethylonitraniline separates as a brown oily mass, which solidifies after some time with crystalline structure. In this substance, as well as in the other ethylated bases, the properties of the mother-compound are only slightly modified. Thus we find in the base ethylonitraniline still the yellow colour of nitraneline, which it readily imparts to the skin, but which it loses altogether in its salts. These salts are as easily soluble in water as the corresponding nitraneline-compounds if not even more so, and possess the same peculiar sweetish taste; they all crystallize, however, on evaporating their solutions nearly to dryness. Ethylonitraniline dissolves readily in ether and alcohol, less so in boiling water; from a solution in the latter the base is deposited in stellated groups of yellow crystals, which are readily distinguished from the felted mass of long needles, separated on cooling from an aqueous solution of nitraneline.

I have fixed the composition of ethylonitraniline by a single number, namely, by the determination of the metal in the platinum double salt. This compound is prepared by adding bichloride of platinum to a very concentrated solution of the hydrochlorate; this

\* Chem. Soc. Mem. II, 291.

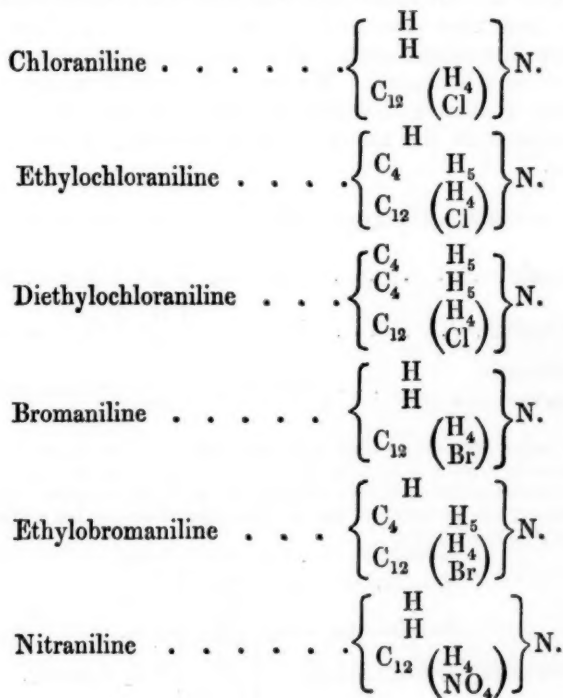
must not contain much free acid, in which the salt would redissolve. After a short time pale-yellow scales are separated, which have to be washed with cold water. Composition :

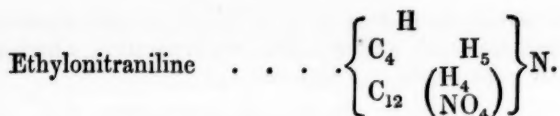


The nitraniline-salt contains 28.66 per cent of platinum. I have not prepared a diethylonitraniline.

The deportment of chloraniline, bromaniline, and nitraniline with bromide of ethyl, appears to throw much light upon the constitution of these substitution-bases. The possibility of introducing into these substances 2 equivalents of ethyl, shows that they must contain the same amount of basic hydrogen (an expression by which I may be allowed to represent briefly the hydrogen of the ammonia-skeleton) as aniline itself, and hence it is evident that it was the hydrogen of the phenyl which was replaced by chlorine, bromine, and hyponitric acid in the transformation of aniline into its chlorinated, brominated, &c., relatives.

This transformation is due to a secondary substitution, affecting the hydrogen in the radical, which replaced the original ammonia-hydrogen; and the constitution of the substances in question may hence be graphically represented by the following formulæ :





This mode of viewing their constitution is in perfect harmony with the facts at present in our possession, both as regards the deportment of the substitution-anilines, and the substances similarly derived from hydrated oxide of phenyl. Experiment has shown that in aniline 1, 2 or 3 equivalents of hydrogen may be replaced by chlorine, bromine, and probably also by the elements of hyponitric acid.\* In these substances their basic properties gradually diminish with the successive insertions of chlorine or bromine into the compound. Bromaniline still retains a strongly alkaloidal character, which in dibromaniline is so far impaired, that by simple ebullition it is separated from its aqueous saline solutions; tribromaniline, lastly, is a perfectly indifferent compound. Now, if we recollect that in monobrominated and dibrominated phenole (obtained by M. Cahours, by distilling, respectively, bromosalicylic and dibromosalicylic acid), the original character of hydrated oxide of phenyl is gradually altered, and becomes in tribromophenole (bromophenisic acid of M. Laurent) powerfully acid, we cannot be surprised to find that the gradual development of electronegative properties in the radical should affect the nature of a basic system in which it replaces hydrogen. We have two parallel groups of bodies, the chemical character of which is differently affected by the modification induced in the radical existing in both, by the assimilation of bromine.

Hydrated protoxide of phenyl	HO. C <sub>12</sub>	H <sub>5</sub>	O, slightly acid.
Bromophenole . . . . .	HO. C <sub>12</sub>	$\left\{ \begin{array}{c} \text{H}_4 \\ \text{Br} \end{array} \right\}$	O, more so,
Dibromophenole . . . . .	HO. C <sub>12</sub>	$\left\{ \begin{array}{c} \text{H}_3 \\ \text{Br}_2 \end{array} \right\}$	O, more so.
Tribromophenole	HO. C <sub>12</sub>	$\left\{ \begin{array}{c} \text{H}_2 \\ \text{Br}_3 \end{array} \right\}$	O, powerfully acid.
Bromophenisic acid . . . }			

\* At the present moment we have only nitr aniline, but it is scarcely to be doubted that we shall soon become acquainted with the nitro-terms corresponding to dichloraniline and trichloraniline. Recent researches of M. Cahours (Ann. Ch. Phys. [3] XXXVII, 439) on the derivatives of anisole have pointed out the first alkaloid containing 2 equivs. of hyponitric acid.

Anisidine . . . C<sub>14</sub>  $\left\{ \begin{array}{c} \text{H}_9 \\ \text{NO}_4 \end{array} \right\}$  N O<sub>2</sub>.

Nitr anisidine . . C<sub>14</sub>  $\left\{ \begin{array}{c} \text{H}_8 \\ \text{NO}_4 \end{array} \right\}$  N O<sub>2</sub>.

Dinitr anisidine . C<sub>14</sub>  $\left\{ \begin{array}{c} \text{H}_7 \\ (\text{NO}_4)_2 \end{array} \right\}$  N O<sub>2</sub>.

In this series only trinitr anisidine C  $\left\{ \begin{array}{c} \text{H}_6 \\ (\text{NO}_4)_3 \end{array} \right\}$  N O<sub>2</sub> is wanting.



Phenylamine . . . . .	$\left\{ \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12} \text{H}_5 \end{array} \right\}$	N, powerfully basic.
Bromophenylamine . . . . .	$\left\{ \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12}(\text{H}_4) \\ \text{Br} \end{array} \right\}$	N, less so.
Dibromophenylamine . . . . .	$\left\{ \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12}(\text{H}_3) \\ \text{Br}_2 \end{array} \right\}$	N, less so.
Tribromophenylamine . . . . .	$\left\{ \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12}(\text{H}_2) \\ \text{Br}_3 \end{array} \right\}$	N, neutral.

Tribromophenylamine (tribromaniline) is a compound differing in its nature in no way from oxamide. Both these substances are ammonia, whose basic character has been counterbalanced by the insertion of a powerfully electronegative radical in the place of one of the hydrogen-equivalents. These two substances, when subjected to the influence of strong acids, comport themselves in exactly the same manner; they both reproduce ammonia, the one with formation of tribromophenesisic, the other of oxalic acid.

The paragraphs now following are devoted to a brief account of the bases derived from aniline by the insertion of methyl and amyl. I have not, however, followed out the examination of these substances to the same extent, the principle having been in fact sufficiently established by the formation of the ethyl-bodies.

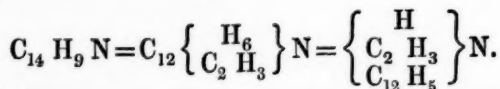
#### ACTION OF BROMIDE AND IODIDE OF METHYL UPON ANILINE.

*Methylaniline (Methylophenylamine).*—The deportment of aniline with bromide of methyl resembles its behaviour with the ethyl-compound. The mixture rapidly solidifies into a crystalline mass of hydrobromate of methylaniline. Bromide of methyl being extremely volatile, I have used also the iodide, which boils at a more convenient temperature. The action of the latter compound upon aniline is very remarkable, the evolution of heat, on mixing the two substances, being so great, that the liquid enters into violent ebullition, so that unless the substances be mixed gradually, the crystalline hydriodate, which is formed immediately, is actually thrown out of the vessel.

Methylaniline, when separated from the hydrobromate or hydriodate, appears as a transparent oil of a peculiar odour, somewhat

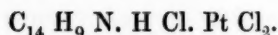
different from that of aniline, and boiling at  $192^{\circ}$ ; it has retained the properties of aniline in a higher degree than the ethylated compound. This substance yields still the blue coloration with hypochlorite of lime, although in a less degree than aniline. Its salts are less soluble than those of ethylaniline; they are at once formed in the crystalline state, on addition of the respective acids; the oxalate crystallizes very easily, but is rapidly decomposed with reproduction of aniline, and probably with formation of oxalate of methyl.

The composition of methylaniline is represented by the expression :



I have established this formula by the analysis of the platinum-salt. This is precipitated as a transparent oil, which rapidly changes into pale-yellow crystalline tufts, resembling the corresponding aniline-salt, but liable to rapid decomposition. The washing must be quickly done, for the salt is extremely soluble in water, and must be immediately followed by desiccation. Even when very carefully prepared, it has become dark by the time it is ready for combustion. It turns instantaneously black if an alcoholic solution of the hydrochlorate be employed for its preparation.

Formula :

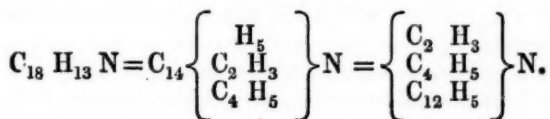


I have not attempted to form a dimethylaniline.

#### ACTION OF IODIDE OF METHYL UPON ETHYLANILINE.

*Methylethylaniline (Methylethylophenylamine).*—I have established the existence of this compound merely by qualitative experiments. The mixture of ethylaniline and iodide of methyl begins to crystallize after two days' exposure to the temperature of boiling water. Methylethylaniline resembles the preceding base in its odour, but has no longer any action upon hypochlorite of lime. I had not prepared a sufficient quantity of the compound for a determination of the boiling-point. The salts of this base are extremely soluble. With the exception of the hydrobromate, I have not been able to obtain a single one in crystals. Even the platinum-salt is not to be obtained in the crystalline form; it is extremely soluble, and separates, if very concentrated solutions be employed, as a yellow oil, which does not solidify even after lengthened exposure to the air. This circumstance has prevented me from fixing the composition of methylethylaniline by a number.

It cannot, however, be doubted that it is represented by the formula



This compound presents a certain degree of interest, inasmuch as the 3 equivs. of hydrogen in the ammonia are replaced by three different radicals, namely, by methyl, ethyl, and phenyl. I have prepared, however, a similar compound containing amyl instead of methyl, whose properties permitted an easier analysis.

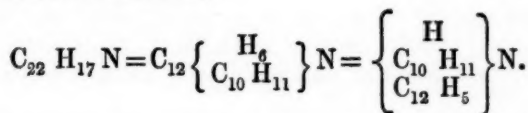
#### ACTION OF BROMIDE OF AMYL UPON ANILINE.

*Amylaniline (Amylophenylamine).*—A mixture of aniline and an excess of bromide of amyl, when left in contact at the common temperature for some days, deposits magnificent crystals of hydrobromate of aniline. Never have I obtained this salt in larger and more definite crystals; although I have seen it deposited of late from a good many solutions. The mother-liquor of this salt is a mixture of amylaniline and bromide of amyl. If aniline be heated in the water-bath, with a very large excess of bromide of amyl, the whole is converted into hydrobromate of amylaniline, which remains dissolved in the excess of bromide.

When prepared without the co-operation of heat, the amylaniline may be purified simply by separating the crystals of the aniline-salt and distilling the remaining mixture, when the bromide of amyl passes over long before the amyl-base begins to volatilize. If the base has been produced by heating the mixture, it is necessary, after the excess of bromide has been removed, to distil the hydrobromate with potassa.

0.2760 grm. of oil gave 0.8161 grm. of carbonic acid, and 0.2560 grm. of water.

Analysis led to the formula:



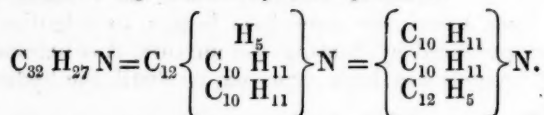
Amylaniline is a colourless liquid, possessing all the family features of the group. It is distinguished, at the common temperature, by a very agreeable, somewhat rose-like odour, rather an unusual property for an amyl-compound; however, it does not deny its origin, for on heating the base, the disgusting odour of the fusel-alcohol appears but slightly modified. Amylaniline boils constantly at 258°, or 54 = 3 × 18° higher than ethylaniline. This boiling-

point is characteristic, inasmuch as the elementary group amyl raises the boiling-point of aniline 44° higher than does the insertion of two equivalents of ethyl, whose weight is not very inferior to that of the single amyl equivalent.

The amyl-base forms beautiful, rather insoluble salts with hydrochloric, hydrobromic and oxalic acids; when heated with water, they form an oily layer on the surface, and crystallize only slowly on cooling: they have the peculiar fatty appearance which characterizes the crystalline amyl-compounds. The platinum-salt is precipitated as a yellow mass of an unctuous consistence; it crystallizes but very slowly, and usually not before partial decomposition has set in. It is on this account that I have not made an analysis of this compound.

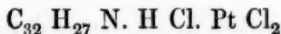
#### ACTION OF BROMIDE OF AMYL UPON AMYLANILINE.

*Diamylaniline (Diamylophenylamine).*—A mixture of amylaniline and bromide of amyl solidifies after two days' exposure to the temperature of the water-bath. The new basic compound, when separated and purified in the usual manner, resembles the preceding base, especially with respect to odour. Its salts are so insoluble in water, that at the first glance one is almost inclined to doubt the basicity of the substance, inasmuch as the oil appears to be perfectly insoluble in dilute hydrochloric and sulphuric acids. However, the oily drops floating in the acid solution are the salts themselves, which gradually solidify into splendid crystalline masses, having likewise the fatty appearance of amyl-substances. The composition of diamylaniline is represented by the expression:



I have established this formula by the analysis of the platinum-compound, which is precipitated as an oily mass, rapidly solidifying into a brick-red crystalline substance. If an alcoholic solution of the hydrochlorate be employed, it is immediately obtained in the crystalline state. When exposed to the heat of the water-bath, this salt fuses, without however undergoing any decomposition.

Formula:

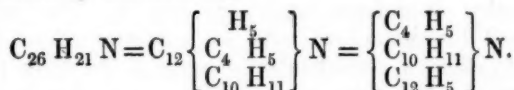


Diamylaniline boils between 275° and 280°; the small scale upon which I had to work prevented me from determining it more accurately. It is interesting to see how very little the boiling-point is raised by the introduction of the second equivalent of amyl, when compared with the effect produced by the insertion of the first. The same remark applies to the ethylanilines.

## ACTION OF BROMIDE OF ETHYL UPON AMYLANILINE AND OF BROMIDE OF AMYL UPON ETHYLANILINE.

*Amylethylaniline (Amylethylophenylamine).*—It remained now only to analyse a basic compound in which the three equivalents of the ammonia-hydrogen should be replaced by three different radicals. I found in amylethylaniline a substance similar in composition to methylethylaniline, but which by its properties admitted of a rigorous analytical examination.

Amylethylaniline is formed without difficulty by the action of bromide of ethyl upon amylaniline. The mixture having been exposed to the heat of the water-bath, the conversion was found to be complete after two days. When purified in the usual way, amylethylaniline forms a colourless oil, boiling at  $262^{\circ}$ , only  $4^{\circ}$  higher than the amyl-base. The properties of this substance are analogous to those of the other bases. It forms a beautiful crystalline hydrochlorate and hydrobromate; the platinum-salt is precipitated in the form of a light orange-yellow pasty mass, which rapidly crystallizes. The salt fuses at  $100^{\circ}$ . By analysis of the platinum-compound, I was enabled to fix without difficulty the composition of the base, which is represented by the formula,



A substance of exactly the same composition as amylethylaniline may be obtained by the action of bromide of amyl upon ethylaniline.

## ACTION OF BROMIDE OF ETHYL UPON AMMONIA.

After the termination of the experiments which have been detailed in the preceding pages, there remained no doubt in my mind respecting the deportment which ammonia itself would exhibit when subjected in a similar manner to the influence of bromide of ethyl. I had a right to expect in this reaction the consecutive formation of three alkaloids, differing from ammonia by containing respectively one, two or the three equivalents of hydrogen replaced by ethyl.

Experiment has realized this expectation in a very satisfactory manner. I intend, to give here only an outline of the process employed, and a short description of the substances obtained.

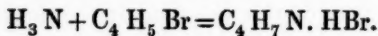
*Formation of Ethylamine (Ethylammonia).*—Bromide of ethyl acts very slowly on an aqueous solution of ammonia in the cold. Action, however, takes place; after the lapse of a week or ten days the solution contains a considerable quantity of a hydrobromate in solution. This hydrobromate is a mixture of the salts of ammonia and ethylamine, the base discovered by M. Wurtz on decomposing cyanate of

ethyl with potassa. The presence of this compound may be readily proved by evaporating the liquid, after the separation of the excess of bromide of ethyl, to dryness in the water-bath, in order to drive off alcohol which might have possibly been formed. On adding potassa-solution to the solid residue, an alkaline gas is at once evolved, which burns with the pale-blue flame of ethylamine.

If an alcoholic solution of ammonia be substituted for the aqueous liquid, the decomposition proceeds more rapidly. After twenty-four hours, a copious crystalline precipitate of bromide of ammonium has been deposited. The mother-liquor contains hydrobromate of ethylamine and the base in the free state.

The action of bromide of ethyl upon ammonia may be considerably accelerated by raising the temperature to the boiling-point of water. I found it convenient to introduce a concentrated solution of ammonia, with an excess of bromide of ethyl, into pieces of combustion-tube 2 feet in length. These tubes, after having been carefully sealed before the blow-pipe, were immersed to the height of about half a foot into boiling water. The bromide of ethyl enters at once into lively ebullition, rises through the supernatant layer of ammonia, condenses in the upper part of the tube, which is cold, and falls down to commence again the same circulation. During this process, the bromide of ethyl diminishes rapidly in volume. The reaction may be considered terminated as soon as a quarter of an hour's ebullition ceases to effect a considerable change in the bulk of the bromide. On opening the tube, the solution is found to be either neutral or even of an acid reaction, and to contain hydrobromate of ethylamine, which may be separated by distillation with potassa, with all the properties enumerated by M. Wurtz. I have not to add a single word to the accurate description of this distinguished chemist, and will here only mention that I have analysed a platinum-salt prepared with ethylamine which had been obtained by this process.

The production of ethylamine in this reaction is absolutely analogous to that of ethylaniline; it is represented by the equation

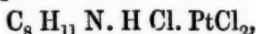


*Formation of Diethylamine (Diethylammonia).*—On treating an aqueous solution of ethylamine in the same manner with an excess of bromide of ethyl, phenomena of a perfectly analogous character are observed. The reaction, however, proceeds more rapidly, and is terminated after a few hours' ebullition. The aqueous layer, which assumes a bright yellow colour, deposits acicular crystals on cooling, consisting of the hydrobromate of a new base, for which I propose the name diethylamine or diethylammonia. This base may be readily separated by distillation with potassa, when it passes over in the form of a very volatile and inflammable liquid, which is still extremely soluble in

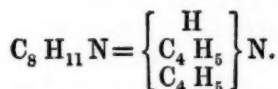


water and of a powerful alkaline reaction. When dissolved in hydrochloric acid and mixed with a concentrated solution of bichloride of platinum, it yields a very soluble platinum-salt, which crystallizes in orange-red grains, very different from the orange-yellow leaves of the corresponding ethylamine-salt.

The analysis of this platinum-salt led to the formula

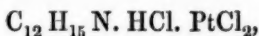


establishing the composition of diethylamine, which is represented by the formula

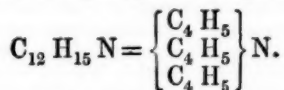


*Formation of Triethylamine (Triethylammonia).*—This arises from diethylamine in the same manner as the latter from ethylamine: however unlike the deportment observed in the formation of diethylaniline, the rapidity of the action increases with the progress of the ethylation. A mixture of a concentrated solution of diethylamine with bromide of ethyl solidifies after a very short ebullition into a mass of beautiful fibrous crystals, sometimes of several inches in length, being the hydrobromate of a new base, for which I propose the name of triethylamine or triethylammonia. This alkaloid may be readily separated by distillation with potassa, when it presents itself in the form of a light, colourless, powerfully alkaline liquid, still very volatile and inflammable, and also pretty soluble in water, but in a less degree than diethylamine.

To fix the composition of triethylamine, the platinum-salt was subjected to analysis. This is one of the finest salts I have ever seen. It is extremely soluble in water, and crystallizes on the cooling of concentrated solutions in magnificent orange-red rhombic crystals, which are obtained of perfect regularity and of very considerable size (half an inch in diameter), even if very limited quantities of solution be employed. The analysis of this salt, which slightly fused at  $100^\circ$ , leads to the formula



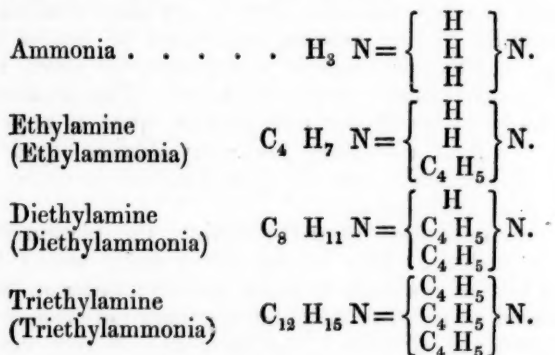
and shows that triethylamine may be considered as ammonia, in which the 3 eqivs. of hydrogen are replaced by 3 of ethyl:



Although not inclined to expect a further action of bromide of ethyl upon triethylamine, after the experiments performed with diethylaniline, but hoping to obtain in this series more definite results than

the latter had yielded, I thought it important to appeal once more to experiment. A mixture of an aqueous solution of triethylamine and bromide of ethyl, sealed for this purpose into a tube, solidified after two hours' ebullition. The crystals formed in this reaction had the fibrous aspect of the hydrobromate of triethylamine; still among the transparent prisms some white opaque granular crystals were observed. To gain more positive information, the excess of bromide of ethyl was volatilized and the residue distilled with potassa. The base obtained in this manner, converted into a platinum-salt and submitted in this form to analysis, gave exactly the percentage of platinum contained in the salt of triethylamine. Accordingly the base which had distilled over, had evidently not been affected any further by the influence of bromide of ethyl. The appearance, however, of the opaque crystals\* indicates that a second compound is formed, whose careful study is necessary for the elucidation of this reaction. I am at present engaged with this part of the inquiry.

The action then of bromide of ethyl upon ammonia gives rise to the formation of the following series of compounds:



It cannot be doubted for a moment that the same compounds will be obtained in the methyl- and amyl-series, the first terms in each of these series having been actually prepared by M. Wurtz. Nor is it improbable that arseniетted and phosphoretted hydrogen, which, as is well known, imitate to a certain extent the habits of ammonia, when

\* I have since ascertained that these white opaque crystals are the hydrobromate of a new base of very remarkable properties. The salt in question may be considered as bromide of ammonium, in which all the hydrogen equivalents are replaced by a corresponding number of ethyl-equivalents. The reaction is much more powerful if instead of bromide of ethyl the iodide be employed. A mixture of triethylamine and iodide of ethyl solidifies at once to a beautiful crystalline salt, containing a base, which may be considered as oxide of ammonium in which the four hydrogen-equivalents are replaced by ethyl. This substance is solid and resembles potassa and soda in its general properties.

subjected to the action of the chlorides, bromides or iodides of the alcohol-radicals, will yield a series of arseniетted or phosphoretted bases, corresponding to the three classes observed with nitrogen. The highly remarkable bodies discovered by M. Paul Thenard appear to warrant this expectation as far as the phosphorus-series is concerned, his compound



corresponding evidently in the phosphoretted methyl-series to triethylamine. I mean to extend these researches to the action of the bromides of the alcohol-radicals on phosphoretted and arseniетted hydrogen.

RELATION OF THE BASES DERIVED FROM ANILINE AND AMMONIA  
WITH OTHER GROUPS OF ALKALOIDS.

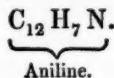
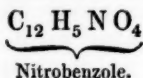
It is impossible to leave the history of these compounds without alluding to some remarkable relations existing between these substances and other bodies of an analogous character, whose constitution is likely to be illustrated by this line of researches. The basic substances derived from aniline, when expressed in formulæ excluding any peculiar view respecting the mode in which the elements are arranged, present a series which is exhibited in the following synoptical table :

Aniline . . . . .	$\text{C}_{12} \text{H}_7 \text{N}$	
Methylaniline . . . . .	$\text{C}_{14} \text{H}_9 \text{N}$	$= \text{C}_{12} \text{H}_7 \text{N} + \text{C}_2 \text{H}_2$
Ethylaniline . . . . .	$\text{C}_{16} \text{H}_{11} \text{N}$	$= \text{C}_{12} \text{H}_7 \text{N} + 2 \text{C}_2 \text{H}_2$
Methylethylaniline . . . . .	$\text{C}_{18} \text{H}_{13} \text{N}$	$= \text{C}_{12} \text{H}_7 \text{N} + 3 \text{C}_2 \text{H}_2$
Diethylaniline . . . . .	$\text{C}_{20} \text{H}_{15} \text{N}$	$= \text{C}_{12} \text{H}_7 \text{N} + 4 \text{C}_2 \text{H}_2$
Amylaniline . . . . .	$\text{C}_{23} \text{H}_{17} \text{N}$	$= \text{C}_{12} \text{H}_7 \text{N} + 5 \text{C}_2 \text{H}_2$
Ethylamylniline . . . . .	$\text{C}_{26} \text{H}_{21} \text{N}$	$= \text{C}_{12} \text{H}_7 \text{N} + 7 \text{C}_2 \text{H}_2$
Diamylniline . . . . .	$\text{C}_{32} \text{H}_{27} \text{N}$	$= \text{C}_{12} \text{H}_7 \text{N} + 10 \text{C}_2 \text{H}_2$

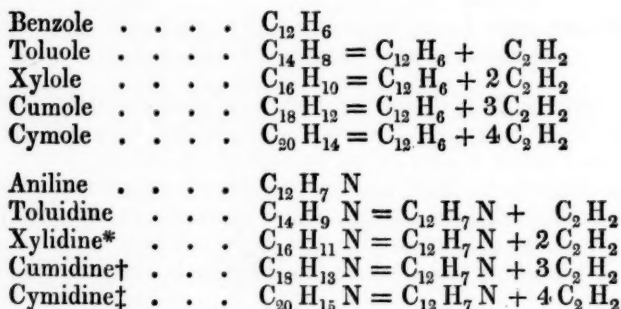
This table shows that the alkaloids in question differ from each other by  $n \text{C}_2 \text{H}_2$ , the elementary difference of the various alcohols and their derivatives; we perceive, moreover, that the series ascends regularly up to the term  $\text{C}_{12} \text{H}_7 \text{N} + 5 \text{C}_2 \text{H}_2$ , when the compound  $\text{C}_{12} \text{H}_7 \text{N} + 6 \text{C}_2 \text{H}_2$  is wanting; lastly, we miss the terms  $\text{C}_{12} \text{H}_7 \text{N} + 8 \text{C}_2 \text{H}_2$  and  $\text{C}_{12} \text{H}_7 \text{N} + 9 \text{C}_2 \text{H}_2$ . The first gap might be easily filled by submitting amylniline to the action of iodide of methyl, methylamylniline being in fact  $\text{C}_{24} \text{H}_{19} \text{N} = \text{C}_{12} \text{H}_7 \text{N} + 6 \text{C}_2 \text{H}_2$ . The other wanting terms cannot be reached from aniline before some of the missing alcohols are discovered.

On examining more closely the formulæ of the preceding conspectus, we find several of them represent basic compounds previously

known. Chemists are acquainted with the beautiful reaction by which Zinin first linked aniline to benzole through nitrobenzole.



Researches performed in the most different departments of organic chemistry have gradually elicited a series of carbohydrides differing from benzole by  $n\text{C}_2\text{H}_2$ ; and each of these terms, when treated with nitric acid, and subsequently exposed to the action of reducing agents, has yielded its corresponding base. We are now in the possession of the following series of alkaloids derived from hydrocarbons:



On comparing the formulæ of the bases contained in the last table with those representing the alkaloids derived from aniline by the introduction of methyl and ethyl, we find that they exactly coincide. Toluidine has the same composition as methylaniline; xylidine, cumidine and cymidine are represented by the same formulæ as ethylaniline, methylethylaniline and diethylaniline. The question then arises, are these substances identical, or are they only isomeric with each other? I have carefully compared the properties of toluidine with those of methylaniline, and also methylethylaniline with cumidine. These substances are not identical, but only isomeric. The most striking dissimilarity we observe in the characters of toluidine and methylaniline. The former is a beautiful crystalline compound, boiling at  $198^\circ$ , yielding difficultly soluble, perfectly stable salts with almost all acids, and a splendid orange-yellow platinum-salt, which may be boiled without decomposition. We are unacquainted with any process by which we could convert this body into aniline. Methylaniline, on the other hand, is an oily liquid,

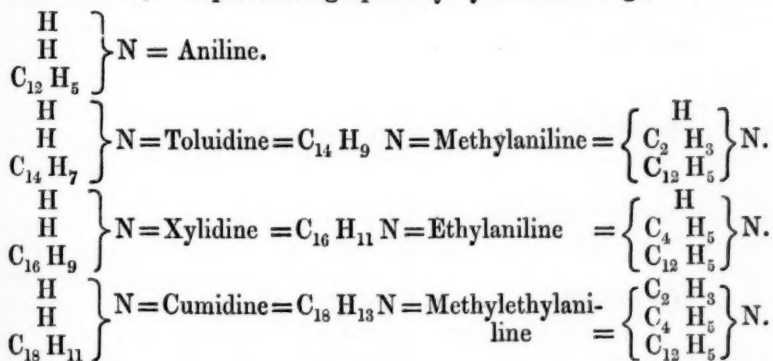
\* Chem. Soc. Qu. J. III, 183.

† On Cumidine, a new Organic Base, by E. Chambers Nicholson; Chem. Soc. Qu. J. I, 2.

‡ This compound has been partly investigated by Mr. Noad.

boiling at  $192^{\circ}$ , whose salts are distinguished by their solubility and by the facility with which they are decomposed, aniline being reproduced. The platinum-salt, even when freshly precipitated, is of a pale yellow colour, which immediately darkens, turning perfectly black after the lapse of an hour. Scarcely less striking is the dissimilarity of cumidine and methylethylaniline, although in this case both substances are liquids. For details I refer to Mr. Nicholson's\* paper on cumidine, and to what I have stated about methylethylaniline. The quantity of this substance I had at my disposal was not sufficient for a determination of the boiling-point; but if we recollect that ethylaniline boils at  $204^{\circ}$ , and that the introduction of methyl into aniline raised its boiling-point about  $10^{\circ}$ , it is evident that methylethylaniline cannot boil at a temperature much higher than  $214^{\circ}$ , *i. e.* eleven degrees below  $225^{\circ}$ , the boiling-point of cumidine observed by Mr. Nicholson. A detailed account of the properties of xylidine has not yet been published; however, I have not the slightest doubt that M. Cahours will find them widely differing from those of ethylaniline.

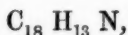
Toluidine, xylidine and cumidine, resembling aniline, not only in their physical characters, but also in their origin from carbohydrides, evidently belong to the class of alkaloids for which I have provisionally retained the name amidogen-bases, while the basic compounds derived from aniline are either imidogen- or nitrile-bases. The difference of properties depends upon a difference in the molecular construction, as represented graphically by the following table:—



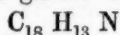
The view which I propose in the preceding remarks respecting the constitution of toluidine, xylidine and cumidine, must as yet be considered as a mere hypothesis. It will not however be difficult to establish it by facts. The action of bromide of ethyl upon these substances will at once decide this question. These bases, when subjected to the influence of the bromides, will give rise to the for-

\* Chem. Soc. Qu. J. I, 4, 5.

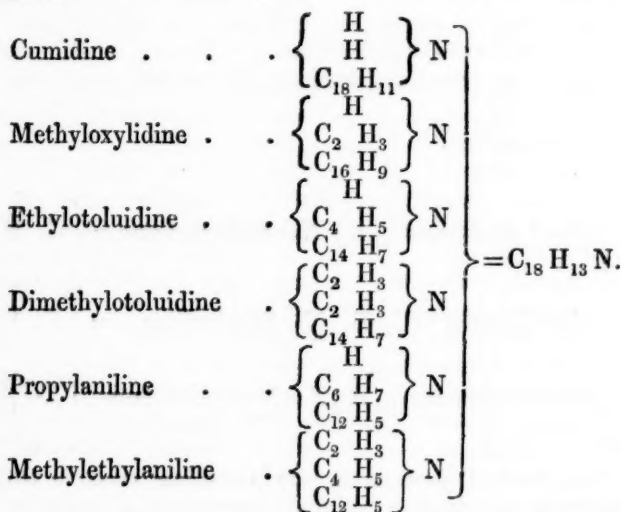
mation of a series of bases similar to those which I have obtained from aniline. I may mention that the deportment of toluidine and cumidine, in this respect, is now being studied by several of my pupils. There is no difficulty in introducing 1 equiv. of ethyl into toluidine; the experiments are, however, not yet sufficiently advanced to affirm also the insertion of the second equivalent. The alkaloid obtained by acting with bromide of ethyl upon toluidine is represented by the formula,



so that we are now in possession of three alkaloids of exactly the same composition, namely, ethyltoluidine, methylethylaniline and cumidine; and here I cannot but allude to the wonderful variety of isomeric compounds to which a continuation of these researches must necessarily lead. We see at a glance that substances of the formula



will also be obtained by inserting 1 equiv. of methyl into xyloidine, by introducing 2 equivs. of methyl into toluidine, or by fixing upon aniline the radical (propyl) belonging to the missing alcohol of propionic acid\* (metacetic acid). We thus arrive at six alkaloids, having all the same numerical formulæ, but widely differing in their construction.



This multiplicity of course augments in the same measure as we

\* A more appropriate name for metacetic acid, proposed by Dumas, Malaguti and Leblanc (Compt. Rend. XXV, 656), as it is the *first* acid of the series  $\text{C}_n \text{H}_n \text{O}_4$  that exhibits the character of a *fatty* acid, *i. e.* in being separated from solution as a layer of oil, and in forming salts with the alkalies that have a greasy appearance.



ascend upon the scale of organic compounds. For every step, the number of possible isomeric bases increases by two, so that on arriving at the term diamylaniline,



being the last member (*vide* p. 298) in the aniline-series which I have examined, we find that its numerical formula actually represents not less than twenty different alkaloids which the progress of science cannot fail to call into existence,—a striking illustration of the simplicity in variety that characterizes the creations of organic chemistry.

Not less numerous will be the isomerisms in the series of bases derived by the insertion into ammonia of the alcohol-radicals  $\text{C}_n \text{H}_{n+1}$  only, as soon as the group of these alcohols themselves shall be more completely known. Ethylamine is isomeric with dimethylamine; diethylamine has the same composition as methylopropylamine, a base containing ethyl and propyl, the alcohol-radical in the propyl series, as dimethylethylamine, and lastly, as butylamine. Some chemists are actually inclined to consider as such a volatile alkaloid discovered by Dr. Anderson\* among the products of the distillation of animal substances, and described by him under the name of petinine. The formula established by Dr. Anderson is



but it is not unlikely that on repeating the analysis an additional hydrogen-equivalent will be found. The boiling-point of the compound ( $75^\circ$ ) is very much in favour of butylamine.

In a similar manner, a great number of bases identical in composition with triethylamine will soon be found,—caproylamine, methylamine, ethylobutylamine, dipropylamine, and a number of others.

In conclusion I append a synoptical view of the various basic compounds which I have derived from ammonia; this will exhibit the chief results of these researches perhaps better than would a brief recapitulation of the several facts.

\* Transactions of the Royal Society of Edinburgh, XVI, 4.

TYPE.	AMIDOGEN-BASES.	IMIDOGEN-BASES.	NITRILE-BASES.
	$\left[ \begin{array}{c} \text{Aniline} \\ \text{(Phenylamine)} \end{array} \right] \left\{ \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12} \text{H}_6 \end{array} \right\} \text{N.}$	$\left[ \begin{array}{c} \text{Ethylaniline} \\ \text{(Ethylphenylamine)} \\ \text{Methylaniline} \\ \text{(Methylphenylamine)} \\ \text{Amylaniline} \\ \text{(Amylphenylamine)} \end{array} \right] \left\{ \begin{array}{c} \text{H} \\ \text{C}_4 \text{H}_5 \\ \text{C}_{12} \text{H}_5 \\ \text{C}_2 \text{H}_5 \\ \text{C}_{12} \text{H}_5 \\ \text{C}_{10} \text{H}_{11} \\ \text{C}_{13} \text{H}_5 \end{array} \right\} \text{N.}$	$\left[ \begin{array}{c} \text{Diethylaniline} \\ \text{(Diethylphenylamine)} \\ \text{Methylethylaniline} \\ \text{(Methylethylphenylamine)} \\ \text{Diamylaniline} \\ \text{(Diamylphenylamine)} \\ \text{(Ethylamylaniline)} \\ \text{(Ethylamylphenylamine)} \\ \text{Diethylchloraniline} \\ \text{(Diethylchlorophenylamine)} \end{array} \right] \left\{ \begin{array}{c} \text{C}_4 \text{H}_5 \\ \text{C}_4 \text{H}_5 \\ \text{C}_2 \text{H}_5 \\ \text{C}_4 \text{H}_5 \\ \text{C}_{12} \text{H}_{11} \\ \text{C}_{10} \text{H}_{11} \\ \text{C}_4 \text{H}_5 \\ \text{C}_{12} \text{H}_{11} \\ \text{C}_4 \text{H}_5 \\ \text{C}_4 \text{H}_5 \\ \text{C}_{12} \text{(Cl)} \end{array} \right\} \text{N.}$
Ammonia (Amine)	$\left[ \begin{array}{c} \text{Chloraniline} \\ \text{(Chlorophenylamine)} \\ \text{Bromaniline} \\ \text{(Bromophenylamine)} \\ \text{Nitraniline} \\ \text{(Nitrophenylamine)} \\ \text{Ethylaniline} \\ \text{(Ethylammonia)} \end{array} \right] \left\{ \begin{array}{c} \text{H} \\ \text{H} \\ \text{C}_{12} \text{(Cl)} \\ \text{H} \\ \text{H} \\ \text{C}_{12} \text{(Br)} \\ \text{H} \\ \text{H} \\ \text{C}_{12} \text{(NO}_2\text{)} \\ \text{H} \\ \text{H} \\ \text{H}_5 \end{array} \right\} \text{N.}$	$\left[ \begin{array}{c} \text{Ethylchloraniline} \\ \text{(Ethylchlorophenylamine)} \\ \text{Ethylbromaniline} \\ \text{(Ethylbromophenylamine)} \\ \text{Ethylonitraniline} \\ \text{(Ethylonitrophenylamine)} \\ \text{Diethylaniline} \\ \text{(Diethylammonia)} \end{array} \right] \left\{ \begin{array}{c} \text{H} \\ \text{C}_4 \text{(H}_4\text{)} \\ \text{C}_{12} \text{(Cl)} \\ \text{H} \\ \text{C}_4 \text{(H}_4\text{)} \\ \text{C}_{12} \text{(Br)} \\ \text{H} \\ \text{C}_4 \text{(H}_4\text{)} \\ \text{C}_{12} \text{(NO}_2\text{)} \\ \text{H} \\ \text{C}_4 \text{(H}_4\text{)} \\ \text{C}_4 \text{H}_5 \end{array} \right\} \text{N.}$	$\left[ \begin{array}{c} \text{Triethylaniline} \\ \text{(Triethylammonia)} \end{array} \right] \left\{ \begin{array}{c} \text{C}_4 \text{H}_5 \\ \text{C}_4 \text{H}_5 \\ \text{C}_4 \text{H}_5 \end{array} \right\} \text{N.}$

**On the Nitrogenated Principles of Vegetables, as the Sources of Artificial Alkaloids.**

**By Dr. John Stenhouse, F.R.S.\***

It is well known that several organic alkaloids, such as Aniline, Picoline, Petinine, &c., are obtained in the dry distillation of coal. Now, as coal is of vegetable origin, and these organic alkaloids all contain nitrogen, it is evident that they must be ultimately derived from the azotized principles contained in the plants from which the coal has been formed. Hence it appears probable that those proximate vegetable principles which are rich in nitrogen, such as vegetable albumen, fibrine, legumine, &c., will, when subjected to destructive distillation, yield these same alkaloids, or bodies closely resembling them, in larger quantities than the coal itself,—inasmuch as the powerful agencies to which that substance has been subjected during the course of its formation, must have destroyed a large amount of these azotized principles; and moreover, the great bulk of it is made up of non-azotized matter, the residue of woody fibre, &c., which can contribute nothing to the formation of the alkaloids. By considerations such as these, the author was induced to undertake the researches of which the following is an abstract.

Since vegetable albumen, fibrine, and caseine, are very difficult to obtain in a state of purity, the experiments were made with those parts of plants, chiefly seeds, which contain those principles in the greatest abundance. The first experiment was made with the seeds of the common horse-bean (*Phaseolus communis*), which contain about 22 per cent of azotized matter. The beans were subjected to dry distillation in cast-iron retorts, and the distilled products condensed by a Liebig's condenser. A strongly alkaline liquid was obtained, containing, besides other products, acetone, wood-spirit, acetic acid, empyreumatic oils, tar, a very large quantity of ammonia, and several organic bases. The crude product was treated with a considerable excess of hydrochloric acid; the clear liquid decanted after the tar had settled to the bottom; the tarry residue treated several times with water containing hydrochloric acid; the several acid liquids mixed, and the whole boiled for a couple of hours. By this treatment, the acetone, wood-spirit, and a large proportion of the empyreumatic oils, were either driven off or separated by conversion into resinous matter. The acid liquid was then filtered through charcoal to separate the resins, and afterwards mixed with lime or soda and distilled. The distillate contained a large quantity of ammonia, together with oily bases, the amount of the latter being greatest in the first portions which passed over. The oily liquid was separated from the ammoniacal solution by means of a pipette; neutralized with hydrochloric acid, whereby the neutral oils mixed with the organic bases were left undissolved, and could be separated

by filtration, and the solution supersaturated with carbonate of soda, and distilled in a large retort. The oily bases again passed over, together with a quantity of ammoniacal liquid, from which they were separated by the pipette. An additional quantity was obtained from the weak alkaline liquid which passed over at the latter part of the first distillation, by neutralizing that liquid with hydrochloric acid, concentrating by evaporation, supersaturating with carbonate of soda, and again distilling. The oily bases obtained by these operations were again rectified with water to purify them from the resinous matter which still remained; then repeatedly agitated with strong potash-solution, which dissolved out the remaining portions of ammonia, and formed a solution which could be separated from the oily liquid by means of a funnel; and lastly, dehydrated by repeated agitation during several days with fused hydrate of potash, and subsequent distillation. The first two-thirds of the oily distillate were colourless; the remainder had a yellowish colour, but was likewise rendered colourless by repeated rectification.

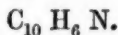
The boiling-point varied considerably during the distillations, showing that the oily liquid obtained was a mixture of different bases. An attempt was therefore made to separate these bases by fractional distillation. The liquid began to boil at  $108^{\circ}$  C., at which point a small portion of a transparent, colourless oil passed over. The thermometer then rose quickly to  $120^{\circ}$ , and from thence to  $130^{\circ}$ , at each of which points small portions were collected. Between  $150^{\circ}$  and  $155^{\circ}$ , the boiling point remained stationary for a considerable time, and a considerable quantity of oil then distilled over; about the same quantity was collected between  $160^{\circ}$  and  $165^{\circ}$ . The boiling-points of the last portions varied between  $165^{\circ}$  and  $220^{\circ}$ . The products of these different distillations were again repeatedly rectified, and by this means bases were obtained corresponding more closely with those points at which the thermometer remained stationary during the first distillation.

These bases, though differing considerably in their boiling-points, nevertheless resemble each other very closely in their other characters. They are colourless, transparent oils, with strong refracting power, lighter than water, and having the peculiar pungent, slightly aromatic odour which is characteristic of this class of bodies. The odour remains on the hands and clothes for a long time, and is strongest and most pungent in those bases which are most volatile. They have a hot taste, not disagreeable in a state of dilution, and resembling that of oil of peppermint. The bases which distil over at low temperatures are tolerably soluble in water,—at any rate, more soluble than those whose boiling-points are high. They all dissolve in every proportion in alcohol and ether. They exhibit strong alkaline reactions with turmeric and reddened litmus-paper, emit copious fumes with hydrochloric acid, and neutralize acids perfectly, generally forming crystallizable salts. With the chlorides of

gold, platinum, and mercury, they form double salts, soluble in water to nearly the same extent as the corresponding ammoniacal salts. They precipitate ferric and cupric salts, the precipitate in the latter case being easily soluble in excess, and yielding a deep blue solution. They do not alter by partial exposure to the air, but if exposed to a strong light, they turn yellow, especially those which boil at the higher temperatures. Nitric acid converts them into yellow resins, but without forming carbazotic acid. With hypochlorite of lime they form brownish resins, but give no trace of aniline. When boiled for a few minutes in a retort, they gradually become coloured, though the liquid which distilled over was colourless at first. At the close of the distillation, a small quantity of resinous matter remained in the retort.

The quantity of these bases obtained was not sufficient to yield any very definite analytical results. It is not that the proportion of bases yielded by beans and other seeds is less than that obtained from animal substances; on the contrary, it is equal to that obtained from bones, and much greater than that yielded by coal: but we have not the advantage—as in the case of bones and coal—of being able to procure the crude oils in large quantity as the waste-products of manufacturing operations; and consequently the chemist is obliged to distil the seeds on purpose, an operation requiring very large apparatus and not conveniently conducted in the laboratory.

The base which boiled between  $150^{\circ}$  and  $155^{\circ}$ , was found by analysis to contain about 74.7 per cent of carbon and 7.98 of hydrogen, numbers which nearly correspond with the formula,



This formula was likewise confirmed by the analysis of the platinum-salt. The combination of this base in the anhydrous state with hydrochloric acid is attended with great evolution of heat. The hydrochlorate is very soluble in water, and crystallizes in slender prisms. Similar compounds are formed with sulphuric and nitric acid. The platinum-salt crystallizes in four-sided prisms arranged in stars of a deep yellow colour. The gold-salt is very soluble in hot water, and crystallizes in pale yellow needles on cooling. The composition of this base approaches very closely to that of nicotine,  $C_{10}H_7N$ ; but its properties agree more nearly with picoline, the base discovered by Dr. Anderson in coal-tar. It has, however, a higher boiling-point, and is less soluble in water than the latter. It is lighter than water, has a peculiar and slightly aromatic odour, and a hot taste resembling peppermint; dissolves in every proportion in alcohol and ether; and remains colourless though kept in an imperfectly stoppered bottle, provided it be not exposed to a strong light. It takes fire readily, and burns with a bright smoky flame.

Three of the bases with which the preceding compound was accom-

panied were likewise analysed and gave the proportions of carbon and hydrogen stated in the following table: (a) is the base, or rather mixture of bases, which boiled between  $160^{\circ}$  and  $165^{\circ}$ ; (b) between  $165^{\circ}$  and  $170^{\circ}$ ; (c) between  $200^{\circ}$  and  $210^{\circ}$ .

	a.	b.	c.
Carbon . . . .	74.08	75.42	75.63
Hydrogen . . . .	8.06	8.52	8.73

It is rather remarkable that the amount of carbon and hydrogen in these bases, or rather mixtures of bases, does not differ more, considering the great difference in their boiling points. They all form double salts with gold and platinum; those which contain the less volatile bases, however, crystallize less readily, and are more contaminated with resinous matter. Their solubility in water likewise diminishes as the boiling-point rises. They all appear to possess equally strong basic properties. More complete investigation was precluded by the great difficulty of procuring these bases in sufficiently large quantity.

The next substance subjected to destructive distillation was oil-cake, or rather the dried seeds of *Linum usitatissimum*, from which the fat oil had been expressed. This substance was selected as the type of that numerous class of plants in which the starch of the *Graminaceæ* is replaced by oil. Of these, the poppy, rape, and mustard are the best known: they are all very rich in albumen. About 2 cwt. of oil-cake was broken into moderate-sized pieces and distilled in the same apparatus as had been used for the beans. The liquid product was smaller in quantity than that obtained from the beans: it had an extremely unpleasant odour, and contained acetone, acetic acid, a large proportion of tar and empyreumatic oils, and a considerable quantity of ammonia. The quantity of organic bases was, however, not more than one-third of that obtained from the beans. The deficiency may, in all probability be attributed to the higher temperature required for the distillation of the oil-cake, inasmuch as the volatile alkaloids are decomposed at high temperatures, with evolution of ammonia.

The bases obtained from the oil-cake were separated and purified by the process already described in the case of the beans. They consisted of a mixture of basic oils different from those yielded by coal or by bones, inasmuch as they contained neither aniline nor quinoline. Their odour was different from that of the bases obtained from beans, but they resembled the latter closely in their basic properties and in the characters of their salts. On the whole it seems probable that some of the bases of the two groups may be identical.

The grain of wheat (*Triticum hybernum*), which was chosen as the type of the *Graminaceæ*, yielded by dry distillation products very different from those previously described—the distillate being strongly acid, from the presence of a large quantity of acetic acid derived



from the starch in the grain. Acetone and wood-spirit were likewise present in considerable quantity. The distillate likewise contained a large quantity of ammonia, but the proportion of organic bases was very small, somewhat less than from oil-cake. These organic bases were very similar to those obtained from the preceding sources, but appeared to be more volatile: they contained neither aniline nor quinoline.

*Peat*, from the moors near Glasgow, when subjected to destructive distillation, yielded a distillate which was nearly neutral, and contained a large quantity of acetic acid, besides acetone and wood-spirit. The acid distillate was mixed with hydrochloric acid and boiled to drive off the acetone and wood-spirit—whereupon, as the liquid cooled, the tarry matter separated as a semi-solid crust on the surface, and could be easily removed. The clear liquid was then supersaturated with carbonate of soda and distilled. An ammoniacal liquid passed over, mixed with a considerable quantity of oily bases which were separated as in former cases. The quantity of these bases was much greater in proportion to the ammonia than in the distillate from the linseed-cake, probably because they distilled over at a lower temperature. They strongly resembled the preceding groups and contained neither aniline nor quinoline.

*Wood*.—The rough distillate of beech, oak, ash, and other hard woods obtained in the manufacture of pyroligneous acid (for which purpose the stems and thicker branches are exclusively employed) was found to contain scarcely a trace either of ammonia or of organic alkaloids. Hence it would appear that the stems of trees are almost destitute of azotized matter, presenting in that respect a striking contrast to peat. This difference may, perhaps, throw some light on the origin of coal. For coal, when subjected to destructive distillation yields a large quantity of azotized products, and must therefore have been formed from vegetable matter rich in nitrogen. Hence the theory which regards it as produced by the submersion of peat-bogs appears to be more probable than that which attributes it to the submersion of trees. It is true that the bases derived from peat are not the same as those from coal; but on the other hand, it must be remembered that plants of different families, when submitted to dry distillation, yield different groups of volatile bases: thus, plants of the indigo tribe yield ammonia and aniline; tobacco-leaves yield ammonia and nicotine, &c., &c. Hence the difference in the distillation-products of peat and coal may perhaps be ascribed to the difference between the plants from which the coal-strata have been formed and those of which the peat-mosses of the present day are composed.

*Formation of Organic Bases from Azotized Vegetable and Animal Substances otherwise than by Destructive Distillation.*

1. *By treating them with alkaline leys*.—A quantity of beans was introduced into a large distillatory apparatus and boiled with caustic

soda. The beans were soon converted into a slimy dark-coloured pulp, which frothed up considerably and rendered the distillation very troublesome. By carefully rectifying the crude distillate, a clear, strongly alkaline liquid was obtained, which contained a large quantity of ammonia, a small quantity of an aromatic oil having an agreeable odour, and a notable quantity of organic bases. These bases were separated in the same manner as in former instances. They were similar to those obtained by destructive distillation, but the author could not positively decide as to whether they were identical. Oil-cake yielded similar results, and hence we may conclude that the same would be the case with the azotized portions of other plants, when similarly treated.

The liver of an ox boiled with caustic soda yielded a strongly alkaline liquid, from which a small quantity of oily bases was obtained, but not sufficient to determine their nature.

2. *By the aid of Sulphuric acid.*—A small quantity of beans was digested with dilute sulphuric acid, care being taken not to let the action proceed so far as to cause the evolution of sulphurous acid. The acid liquid, supersaturated with carbonate of soda and distilled, yielded an ammoniacal distillate containing organic bases similar to those already described. Hence it is probable that animal substances, similarly treated, would likewise yield organic bases.

3. *By Putrefaction.*—A quantity of horse-flesh, previously exhausted of soluble matters by long-continued boiling, was moistened with water and left to itself in a warm place for a month. When it had reached a somewhat advanced state of putrefaction, it was treated with water containing hydrochloric acid as long as anything was dissolved out, and the acid liquid concentrated, filtered, supersaturated with carbon of soda, and distilled. An alkaline liquid passed over, from which, by repeated rectification with caustic soda, a light oily fluid was obtained, consisting of several organic bases mixed together. It had an aromatic and not unpleasant odour, was very soluble in water, strongly alkaline, and formed crystalline salts with acids. Contrary to expectation, however, it was found to be quite free from aniline. The quantity of organic bases obtained from this source was not so great as might have been expected; being much less than that produced by destructive distillation. Perhaps however, if the putrefaction were suffered to go on for a longer time—till, in fact, the flesh should be completely decomposed—the quantity of bases thereby produced might be greater than that resulting from destructive distillation. Considering indeed the very gradual nature of the putrefactive process, it may possibly be found the most advantageous that can be adopted for the preparation of these alkaloids on the large scale.

4. *Organic bases from Guano.*—A quantity of Peruvian guano, very dry, of pale yellow colour, and emitting a comparatively feeble odour, was distilled with water and an excess of quick lime. The

distillate, which was strongly ammoniacal, was saturated with hydrochloric acid, evaporated to one-third of its bulk, then supersaturated with carbonate of soda, and re-distilled. The liquid which passed over contained a small but appreciable quantity of oily bases, which appeared to be more easily soluble in water than those obtained from the preceding sources.

*Bases from Lycopodium.*—A quantity of lycopodium (the reproductive matter of lycopodiaceæ) boiled with strong caustic soda, evaporated to dryness and distilled, yielded a considerable quantity of ammonia, and a basic oil, which was but slightly soluble in water, and had a peculiar, very penetrating odour, like that of the borage plant. It neutralized acids completely, but in other respects did not resemble the bases previously mentioned. The same oil was obtained by destructive distillation of the plant; towards the end of the operation, however, another oily liquid was obtained having an odour more like that of the bodies previously described. This result with lycopodium affords another instance of the fact that plants of different natural families, yield different groups of volatile organic bases.

*Bases from Pteris aquilina.*—The stems and leaves of the common fern (*P. aquilina*) being subjected to distillation, yielded a very alkaline liquid, containing ammonia and a tolerably large quantity of organic bases, the odour of which was very much like that of the bases obtained from beans and from linseed.

From the facts above detailed, it seems to follow that "*Whenever ammonia is produced in large quantity from complex animal or vegetable substances, it is always accompanied by the formation of volatile organic bases.*" If, therefore, researches similar to the above are actively prosecuted, and especially if the seeds and leaves of the various genera of plants are subjected to similar processes, it seems not unreasonable to expect that the number of volatile organic alkaloids will ere long be considerably increased.

Another inference which seems to follow from these experiments is, that the nitrogenous principles of these plants, viz. vegetable albumen, caseine, fibrine, &c., though very analogous to the corresponding principles of the animal kingdom, are not identical with them; otherwise the products of decomposition would be the same.

In conducting the destructive distillation of animal and vegetable substances, it is important to operate at as low a temperature as possible; for if the heat be raised too high, the organic bases are almost totally destroyed, ammonia being then the only alkaline product. It is highly probable that, in many cases, the ammonia obtained in the distillation of animal and vegetable substances is really derived from the destruction of organic bases; for these organic bases are more complex in their structure than ammonia; and the most stable of them, when passed once or twice through a tube filled with red-hot charcoal, are almost entirely converted into

that alkali; and even when organic bases are strongly heated in contact with potash or soda, or when their aqueous solutions are simply boiled for any length of time, they always undergo partial decomposition, ammonia being an invariable product.

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**On the Mechanical Equivalent of Heat.**

**By J. P. Joule, F.C.S.\***

Opinions have long been divided between two hypotheses respecting the nature of heat,—the one regarding it as a peculiar substance, the other as the effect of motion among material particles. The latter hypothesis appears to be most in accordance with the development of heat by friction—a phenomenon first accurately investigated by Count Rumford, who showed that the very great quantity of heat excited in the boring of cannon could not be ascribed to a change in the calorific capacity of the metal, and thence concluded that it was due to the motion in the particles communicated by the borer. “It appears to me,” he remarks, “extremely difficult, if not impossible, to form a distinct idea of anything capable of being excited and communicated, as the heat was communicated in these experiments, except it be motion.”†

In the same paper, Count Rumford makes an estimate of the quantity of mechanical force required to produce a certain amount of heat—showing, in fact, that the friction produced by the power of one horse acting for two hours and a half will generate heat sufficient to raise 26·58 pounds of water from 32° to 212° F. Now, the power of a horse is estimated by Watt at 33,000 foot-pounds,‡ and, therefore, if continued for two hours and a half, will amount to 4,950,000 foot-pounds. Hence it is easily calculated that the heat required to raise a pound of water 1° must be equivalent to the force represented by 1034 foot-pounds. This estimate of the force is rather too high, no account having been taken of the heat communicated to the containing vessel, or of that which was lost by dispersion during the experiment.

About the end of the last century, Sir Humphry Davy showed, that when two pieces of ice were rubbed together *in vacuo*, part of them was melted, although the temperature of the receiver was kept below the freezing-point. This experiment was the more decisive in favour of the doctrine of the immateriality of heat, inasmuch as the heat-capacity of ice is much less than that of water. It was, therefore, with good reason that Davy drew the inference that “the immediate cause of heat is motion, and the laws of its communi-

\* Phil. Trans. 1850, I, 61.

† Phil. Trans. (abridged), XVIII, 286.

‡ A foot-pound is the force expended in raising a pound-weight one foot high in a minute.

cation are precisely the same as the laws of the communication of motion."\*

Dulong discovered the remarkable fact that:—"Equal volumes of all elastic fluids, at the same temperature and under the same pressure, if compressed or dilated suddenly to the same fraction of their volume, disengage or absorb the same absolute quantity of heat."† This law is of the utmost importance in the development of the theory of heat, inasmuch as it shows that the calorific effect is, under certain conditions, proportional to the force expended.

The researches of Dr. Faraday on the relations between light, heat, electricity, magnetism, and chemical force, all tend to show that the so-called imponderables are merely exponents of different kinds of force. Mr. Grove and M. Mayer have likewise advocated the same views.

The earlier investigations of Mr. Joule in connection with this matter are described in his Memoir as follows:

"My own experiments in reference to the subject were commenced in 1840, in which year I communicated to the Royal Society my discovery of the law of the heat evolved by voltaic electricity, a law from which the immediate deductions were drawn: 1st. That the heat evolved by any voltaic pair is proportional, *ceteris paribus*, to the electromotive force;‡ and 2nd. That the heat evolved by the combustion of a body is proportional to the intensity of its affinity for oxygen. I thus succeeded in establishing relations between heat and chemical affinity. In 1843, I showed that the heat evolved by magnetic electricity is proportional to the force absorbed, and that the force of the electromagnetic engine is derived from the force of chemical affinity in the battery, or force which would otherwise be evolved in the form of heat. From these facts I considered myself justified in announcing that the quantity of heat capable of increasing the temperature of a pound of water by one degree of Fahrenheit's scale, is equal to, and may be converted into, a mechanical force capable of raising 838 lbs. to the perpendicular height of one foot."§

"In a subsequent paper, read before the Royal Society in 1844, I endeavoured to show that the heat absorbed and evolved by the rarefaction and condensation of air is proportional to the force evolved and absorbed in those operations.|| The quantitative relation between force and heat deduced from these experiments is almost identical with that derived from the electro-magnetic experiments just referred to, and is confirmed by the experiments of M. Seguin on the dilatation of steam."¶

"From the explanation given by Count Rumford of the heat

\* Elements of Chemical Philosophy, p. 94.

† Mem. Acad. Sec. X, 188.

|| Phil. Mag. XXVI, 375, 379.

‡ Phil. Mag. XIX, 275.

§ Phil. Mag. XXIII, 441.

¶ Compt. Rend. XXV, 421.



arising from the friction of solids, one might have anticipated, as a matter of course, that the evolution of heat would also be detected in the friction of liquid and gaseous bodies. Moreover, there were many facts, such as, for instance, the warmth of the sea after a few days of stormy weather, which had long been attributed to fluid friction. Nevertheless, the scientific world, pre-occupied with the hypothesis that heat is a substance, and following the deductions drawn by Pictet from experiments not sufficiently delicate, have almost unanimously denied the possibility of generating heat in that way. The first mention, so far as I am aware, of experiments in which the evolution of heat from fluid friction is asserted, was in 1842 by M. Mayer,\* who states that he has raised the temperature of water from  $12^{\circ}$  to  $13^{\circ}$  C. by agitating it, without, however, indicating the quantity of force employed or the precautions taken to secure a correct result. In 1843, I announced the fact that 'heat is evolved by the passage of water through narrow tubes,'† and that each degree of heat per pound of water required for its evolution in this way a mechanical force represented by 770 foot-pounds. Subsequently, in 1845‡ and 1847,§ I employed a paddle-wheel to produce the fluid friction, and obtained the equivalents of 781·5, 782·1, and 787·6 respectively, from the agitation of water, sperm-oil, and mercury."

Results so closely in accordance with one another, and with those previously derived from experiments with elastic fluids and the electro-magnetic machine, indicated beyond doubt the existence of an equivalent between force and heat; but still it appeared of the highest importance to obtain that relation with greater accuracy. With this view, fresh experiments were made, of which the following is an abstract:

The apparatus employed for producing the friction of water consisted of a brass paddle-wheel, furnished with eight sets of revolving arms, working between four sets of stationary vanes. This revolving apparatus was firmly fitted into a copper vessel, in the lid of which were two necks, one for the axis to revolve in without touching, the other for the insertion of a thermometer. A similar apparatus, but made of iron, of smaller size, and having six rotatory and eight sets of stationary vanes, was used for experiments on the friction of mercury. The apparatus for the friction of solids consisted of a vertical axis carrying a bevelled cast-iron wheel, against which a fixed bevelled wheel was pressed by means of a lever; the wheels were enclosed in a cast-iron vessel filled with mercury, the axis passing through the lid. In all these arrangements, motion was given to the axis by the descent of leaden weights suspended by strings from the axes of two wooden pulleys, these axes being supported on

\* Ann. Ch. Pharm. XLI.

† Phil. Mag. XXIII, 442.

‡ Phil. Mag. XXVIII, 205.

§ Phil. Mag. XXXI, 173; also Compt. Rend. XXV, 309.



friction-wheels. The pulleys were connected by fine twine passing round their circumferences, with a wooden roller, which, by means of a pin, could be easily attached to or removed from the axis of the frictional apparatus.

The mode of experimenting was as follows:—The temperature of the frictional apparatus having been ascertained, and the weights wound up with the assistance of a stand provided for the purpose, the roller was fixed to the axis. The precise height of the weights above the ground having been determined by means of graduated vertical slips of wood, the roller was set at liberty and allowed to revolve till the weights reached the floor. The roller was then removed to the stand, the weights wound up again, and the friction renewed. After this had been repeated twenty times, the experiment was concluded with another observation of the temperature of the apparatus. The mean temperature of the apartment was determined by observations made at the commencement, middle, and determination of each experiment.

Previously to, or immediately after each experiment, an observation was made of the effect of radiation and conduction to or from the atmosphere, in depressing or raising the temperature of the friction apparatus. In these trials, the position of the apparatus, the quantity of liquid contained in it, the time occupied, the method of observing the thermometers, the position of the experimenter—in short, everything, with the exception of the apparatus being at rest—was the same as in the experiments in which the effect of friction was observed.

In the experiments with water, a correction was made for the quantities of heat absorbed by the copper vessel and the paddle-wheel; and in the experiments with mercury and cast-iron, the heat-capacity of the whole apparatus was determined by ascertaining the heating effect which it produced on a known quantity of water in which it was immersed. In all the experiments, corrections were likewise made for the velocity with which the weights came to the ground, and for the quantity of force expended in overcoming friction and the rigidity of the strings.

The thermometers with which the temperatures were observed had their tubes calibrated and graduated by Regnault's method, and were capable of indicating a difference of temperature as small as  $\frac{1}{100}$  of a degree of Fahrenheit's scale.

*Friction of water.*—A force of 6067·14 foot-pounds was found to raise the temperature of 97470·2 grains of water by 0°·563209, which is equivalent to 7·842299 pounds of water raised 1°. Consequently:

$$\frac{6067 \cdot 114}{7 \cdot 842299} = 773 \cdot 64 \text{ foot-pounds,}$$

is the force, which, according to this determination, is equivalent to 1° Fahr. in a pound of water.

*Friction of mercury.*—In one set of experiments with the mercurial apparatus, a force of 6077·939 foot-pounds was found to generate heat sufficient to raise the temperature of 7·85505 pounds of water one degree; the equivalent thence deduced is :

$$\frac{6077\cdot939}{7\cdot85504} = 773\cdot62$$

A second series of experiments with the same apparatus, but smaller weights, gave for the equivalent :

$$\frac{2100\cdot272}{2\cdot70548} = 776\cdot303$$

*Friction of cast-iron.*—A force of 5980·955 foot-pounds generated heat sufficient to produce a rise of 1° in 7·69753 pounds of water. The equivalent thence deduced is :

$$\frac{5980\cdot955}{7\cdot69753} = 776\cdot997$$

Another series of experiments, with smaller weights, gave :

$$\frac{2057\cdot336}{2\cdot65504} = 774\cdot88$$

In these last experiments, the friction of the cast-iron wheels produced a considerable vibration in the frame-work of the apparatus, as well as a loud sound; it was, therefore, necessary to make allowance for the quantity of force expended in producing these effects.

The following table contains a summary of the equivalents determined as above; in the fourth column the results are given with the correction necessary to reduce them to a vacuum.

Material employed.	Equivalent in air.	Equivalent <i>in vacuo</i> .	Mean.
Water . . . . .	773·640	772·692	772·692
Mercury . . . . .	773·762	772·814	774·083
„ . . . . .	776·303	775·352	
Cast iron . . . . .	776·997	776·045	774·987
„ . . . . .	774·880	774·930	

The equivalent 772·692 is regarded by the author as the most correct; but even this, he observes, is probably a little too high, because, even in the friction of fluids, it is impossible entirely to avoid vibration and the production of a slight sound.

The conclusions to be deduced from all the experiments above-described are :

1. *That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the force expended.*

2. *That the quantity of heat capable of increasing the temperature of a pound of water (weighed in vacuo, and taken at between 55° and 60°) by 1° FAHR., requires for its evolution the expenditure of a mechanical force represented by the fall of 772 lbs. through the space of one foot.*

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Nov. 4, 1850.

THOMAS GRAHAM, Esq., V.P., in the Chair.

The following Donations to the Library have been made since the last Meeting:

"The Pharmaceutical Journal," Vol. X. Nos. 1, 2, 3, 4, and 5: by the Editor.

"Journal of the Franklin Institute," Vol. XIX. Nos. 5 and 6; Vol. XX. Nos. 1 and 2: by the Institute.

"Transactions of the Royal Society of Edinburgh," Vol. IV—XIX; Part 1, Vol. XX.; and the "Proceedings of the Royal Society of Edinburgh," Parts 35—39: by the Society.

"On the Constitution of Codeine and its Products of Decomposition," by Thomas Andrews, M.D.: by the Author.

"Report to General Sir Thomas Macdougall Brisbane, Bart., on the completion of the publication in the Transactions of the Royal Society of Edinburgh, of the observations made in his Observatory at Markerstown," by John Allen Brown: presented by the Author.

"On the Isomorphism and Atomic Volume of some Minerals," by James D. Dana: by the Author.

"Berichte über die Mittheilungen von Freunden der Naturwissenschaften in Wien," von Wilhelm Haidinger. Band V. and VI. 1848—9.

"Bulletin of the Royal Belgian Academy of Medicine," Vol. IX. Nos. 3—7: by the Academy.

"Quarterly Journal of the Geological Society," Vol. VI. No. 23 by the Society.

"Setzungsberichte der Kaiserlichen Akademie der Wissenschaften, Mathematisch - Naturwissenschaftliche Classe." Erste Abtheilung, (Jan. Feb. March, April).

"Haidinger's Report," Vol. V. and VI. 1849—50: by the Society of the Friends of Natural Science in Vienna.

"Abhandlungen der Mathematisch-physikalischen Classe der Königlich Bayerischen Akademie der Wissenschaften." Band V. 1, 2, 3 Abtheilungen.

"Chemical Investigation of the most important Mineral Waters of the Duchy of Nassau," by Dr. R. Fresenius: by the Author.

"Ueber den Antheil der Pharmacie an der Entwicklung der Chemie:" von Dr. Ludwig Buchner, Jun.

"Laurent and Gerhardt's Comptes Rendus," (from Quesneville's "Revue Scientifique"), Nos. 1—9: by M. Quesneville.

"Taylor's Calendar of the Meetings of the Scientific Bodies of London for 1850—1": by the Publisher.

"Silliman's American Journal for September, 1850": by the Editor.

"Quesneville's Revue Scientifique from December 1849 to May, 1850: by M. Quesneville.

"On the Power of Soils to absorb Manure," by Professor Way: by the Author.

"De Cerevisiæ vera Mixtione et indole Chemica, et de Methodo analytica alcoholis quantitatem recte explorandi," scripsit Dr. H. Wackenroder: by the Author.

The following Papers were read:

"On the Magnetic Attraction of Metals," by Mr. Richard Adie, Liverpool.

## XXVII.—*Researches on the Organic Radicals.*

By E. FRANKLAND, PH.D., F.C.S.

### III. ON THE ACTION OF SOLAR LIGHT UPON IODIDE OF ETHYL.

The action of light in modifying and controlling chemical affinity has frequently been the subject of investigation, and the exceedingly curious and interesting results which have already been observed, seem to promise that this agent will become a most valuable assistant in chemical research. Gay-Lussac and Thénard were the first to point out, that chlorine and hydrogen may be preserved in contact for any length of time, without entering into combination, if the mixture be carefully preserved from light; but that with the presence of light, combination immediately commences, and proceeds with a rapidity proportional to the luminous influence. According to Faraday, iodine and olefiant gas combine most readily in sunshine; and the name phosgene gas was given to chlorocarbonic acid, because light was found to be essentially necessary to its formation. These are a few of the instances in which light has been observed to produce direct combination; but the cases in which it effects decomposition and changes the order of elective affinity, are much more numerous.

Under the influence of light, chlorine is enabled to decompose water, uniting with its hydrogen, and liberating pure oxygen gas; and, according to Grothuss, the blue solution of iodide of starch

in water is completely decolorized with the production of hydriodic acid. Scheele, Seebeck, and others, found that nitric acid, exposed to sunlight, is converted into nitrous acid and oxygen, whilst many metallic oxides lose the whole or a part of their oxygen: thus, peroxide of lead is resolved into minium and oxygen; grey oxide of mercury into metallic mercury and red oxide; whilst red oxide of mercury, under water, is decomposed into grey oxide and oxygen gas. Oxide of silver is resolved into silver and oxygen; carbonate of silver into silver, oxygen, and carbonic acid; and oxide of gold into gold and free oxygen. Boullay finds that aqueous solution of perchloride of mercury is decomposed into protochloride of mercury, hydrochloric acid, and oxygen gas. In addition to these curious reactions, the highly interesting and important discoveries of Hunt, Daguerre, Herschell, and Talbot, need only be mentioned to establish the great scientific, as well as practical, importance of this remarkable function of light, which is also so completely under the control of the operator, admitting of being increased, diminished, or modified at pleasure, that there seems every probability of this agent becoming one of our most valuable means of composing, decomposing, and ascertaining the rational constitution of organic bodies, especially as it allows of being applied in such a convenient manner, and under circumstances in which other means are inapplicable.

It has been long known that certain inorganic bodies, containing iodine, such, for instance, as the iodides of silver and gold, undergo decomposition when exposed to light, the iodine compounds of the noble metals appearing to be most susceptible of this change. From the close relation of hydrogen to these metals, its iodide might be expected to possess the same susceptibility, and this is, in fact, found to be the case; for it is well known that aqueous hydriodic acid, even when preserved in closely stopped bottles, gradually turns brown on exposure to light, from the separation of free iodine, but the decomposition only becomes continuous when the iodine is removed as fast as it is liberated; it has also been observed, that when hydriodic acid gas is allowed to stand over mercury, its volume becomes reduced to one half, and the residual gas consists of pure hydrogen; but whether this reaction only occurs under the influence of light, has not yet been clearly established.

In a former memoir,\* I pointed out the very close analogy existing between the functions of the compound alcohol-radicals, and those of the simple radical hydrogen, as exhibited, firstly, in the constitution

\* Chem. Soc. Qu. J. III, 47.

of the vapours of their parallel compounds; secondly, in the decomposition of their respective iodides by zinc; and, thirdly, in the replacement of hydrogen by methyl, ethyl, amyl, &c., in cacodyl, in the new nitrogenous bases of Wurtz and Hofmann, and in those of M. Paul Thénard containing phosphorus. In order to add another link to the chain of evidence which already exists in support of this analogy, it appeared interesting to ascertain if the action of light upon the iodides of ethyl, methyl, &c., would yield results corresponding to those obtained from iodide of hydrogen under similar circumstances; and this link seemed to me also of greater importance, on account of the results thus produced by the simple action of an imponderable agent, being less likely to be influenced by the formation of secondary compounds, than in the action of zinc upon these bodies at an elevated temperature. My experiments have as yet been principally confined to the iodide of ethyl, and it is the results of the action of light upon this body, that I have now the honour to communicate to the Society.

It has been remarked by almost all chemists who have had occasion to employ iodide of ethyl, that this liquid slowly becomes brown, from the separation of iodine, when exposed even to diffused daylight; this observation, which I have myself of late also frequently had an opportunity of making, induced me to hope that a decomposition here occurs analogous to that suffered by iodide of hydrogen under the same influence. I find that the ethyl-compound, when exposed to direct solar light, rapidly becomes of a dark-brown colour; but, as is the case with hydriodic acid, this separation of iodine soon ceases, and when a certain intensity of colour has been attained, no further action takes place; if, however, the free iodine be removed by agitating the liquid with mercury, the action immediately recommences, and proceeds to the same point as before. This behaviour of the iodide under the influence of light, and in contact with mercury, indicated the method by which the action could be carried on continuously, and the products collected and preserved.

For this purpose, several glass flasks, of about 10 ounces capacity, were filled with mercury, and inverted in a vessel containing the same metal; a few drops of iodide of ethyl being then introduced into each, by means of a pipette, they were exposed to the direct rays of the sun. The surface of the mercury, where it was in contact with the liquid, soon became covered with a film of protoiodide, which, by the further action of the light, was converted into biniodide, whilst bubbles of gas were continually evolved, and gradually displaced the mercury from the flask: finally, the whole of the iodide



of ethyl disappeared, the gas and biniodide of mercury being the sole products of the decomposition. Although simple exposure to the sun's rays caused this action to take place with tolerable rapidity, yet it was very greatly accelerated by placing each flask near the focus of an 18-inch parabolic reflector, which was not, however, so highly polished as to cause a very considerable elevation of temperature, the heat never rising to the boiling-point of iodide of ethyl ( $71.6^{\circ}$  C.): in this manner, a few hours' exposure sufficed to fill the flasks with gas, which was then transferred to the bell-glass figured in a former Memoir,\* and allowed to stand over sulphuretted water for twelve hours. At the end of this time, all traces of iodide of ethyl vapour had been absorbed, and the gas was fit for the endiometrical operations.

As iodide of ethyl is not in the least acted upon by mercury at a temperature of  $150^{\circ}$  C.,† it could scarcely be supposed that the comparatively low degree of heat to which these materials were exposed in the focus of the reflector, could play any important part in the decomposition; yet, in order to set this question entirely at rest, an inverted bell-jar containing iodide of ethyl confined over mercury, was surrounded by a glass cylinder, and this latter filled first with water, then with a solution of chloride of copper, and lastly, with a solution of bichromate of potash. When the outer cylinder was filled with water, the decomposition proceeded with as much rapidity as without the intervention of that fluid, whilst the temperature of the water was scarcely perceptibly raised during the operation; the same was the case when solution of chloride of copper was employed; but on substituting the solution of bichromate of potash, scarcely the slightest action was perceptible, even after several days' exposure to bright sunshine. Now since, according to Mr. Hunt, at whose suggestion I employed these liquids, the solution of chloride of copper absorbs nearly all the heating rays, and allows about 90 per cent of the actinic rays to pass, whilst the solution of bichromate of potash intercepts the actinic and gives free passage to the heating rays, it is evident that the decomposition before us is due to the chemical influence of light, and is totally independent of the heating rays of the solar spectrum.

The gas collected and preserved as just stated, was then submitted to the eudiometrical processes, minutely described in my former Memoir on the "Isolation of Ethyl,"‡ the observations were also made with similar precautions respecting temperature, pressure, and formation of nitric acid, during the explosion with excess of oxygen.

\* Chem. Soc. Qu. J. II, 266.

† Chem. Soc. Qu. J. II, 269.

‡ Chem. Soc. Qu. J. II, 295.

The entrance of atmospheric nitrogen into the gas, during the time occupied in its purification from iodide of ethyl vapour, by standing over sulphuretted water, was sought to be avoided by using a deep bell-jar of comparatively small diameter, and an outer glass cylinder,\* having its internal diameter only  $\frac{1}{4}$  inch greater than the external diameter of the interior jar; thus a very small surface of liquid was exposed to the atmosphere, and, therefore, only a proportionably small amount of nitrogen could be absorbed, and transferred to the internal gas. The experiments detailed below, show that the plan was effectual, as none of the gases examined contained an appreciable amount of that element.

A determination of the specific gravity of the gas gave the following numbers :

Temperature of room	.	.	.	24.3° C.
Height of barometer	.	.	.	767.6 mm.
Height of inner column of mercury	.	.	.	13.6 „
Weight of flask and gas	.	.	.	31.6758 grms.
Temperature in balance-case	.	.	.	25.3° C.
Weight of flask filled with dry air	.	.	.	31.5559 grms.
Temperature in balance-case	.	.	.	25.7° C.
Capacity of flask	.	.	.	140.79 cbc.

From these data the specific gravity was calculated to be 1.7159.

To ascertain the composition of the gas, it was first subjected to the action of fuming sulphuric acid; two specimens were then exploded with atmospheric air and excess of oxygen, and the residue was treated with recently boiled absolute alcohol. The following numbers were obtained :

#### In absorption eudiometer.

##### I.

	Observed vol.	Temp.	Difference of mercury level.	Barom <sup>r</sup> .	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Vol. of gas used (dry).	175.4	24.4° C.	6.3 <sup>mm</sup>	761.0 <sup>mm</sup>	121.51
Vols. after action of SO <sub>3</sub> (dry).	150.6	19.5° „	19.0 „	759.5 „	104.08
Vol. after removal of specimen for combustion.	86.9	19.8° „	62.1 „	766.3 „	57.05
Vol. after absorp- tion by alcohol.	0.0	—	—	—	0.00

\* See Fig. 2. *BB*, Chem. Soc. Qu. J. II, 266.

## In combustion eudiometer.

## II.

	Observed vol.	Temp.	Difference of mercury level.	Barom <sup>r</sup> .	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Vol. of gas used (moist). }	94.8	17.4°C.	601.0 <sup>mm</sup>	764.8 <sup>mm</sup>	13.24
Vol. after admission of air (moist). }	472.2	17.7° „	200.3 „	764.4 „	243.45
Vol. after admission of O (moist). }	567.0	17.9° „	112.8 „	763.9 „	338.30
Vol. after explosion (moist). }	525.7	18.1° „	150.5 „	763.6 „	294.66
Vol. after absorption of CO <sub>2</sub> (dry). }	467.8	16.4° „	204.7 „	765.2 „	247.34
Vol. after admission of H (dry). }	683.3	17.3° „	11.9 „	765.7 „	484.36
Vol. after explosion (moist). }	517.9	17.7° „	157.5 „	765.1 „	288.16

## III.

	Observed vol.	Temp.	Difference of mercury level.	Barom <sup>r</sup> .	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Vol. of gas used (moist). }	98.2	17.3°C.	595.4 <sup>mm</sup>	764.9 <sup>mm</sup>	14.29
Vol. after admission of air (moist). }	511.9	17.6° „	161.5 „	764.7 „	282.85
Vol. after admission of O (moist). }	602.9	18.1° „	85.1 „	764.8 „	375.53
Vol. after explosion (moist). }	559.8	18.2° „	123.6 „	765.3 „	328.57
Vol. after absorp- tion of CO <sub>2</sub> (dry). }	501.9	17.0° „	176.2 „	764.4 „	277.90

Analysis No. I. proves that the gas is a mixture, and contains in 100 parts :

Gas absorbable by SO <sub>3</sub> . . . .	14.34
Gas unabsorbable by SO <sub>3</sub> . . . .	85.66
	<hr/>
	100.00

And the perfect disappearance of the gas left unabsorbed by sulphuric acid, on subsequent treatment with about an equal volume of absolute alcohol, proves the absence of hydrogen and hydride of methyl (light

carburetted hydrogen), as also any appreciable amount of nitrogen, which might have permeated the sulphuretted water used to confine it during purification.

Analysis No. II. shows that 13.24 vols. of the gas remaining after the action of fuming sulphuric acid, consumed 77.72 vols. oxygen, and generated 47.32 vols. carbonic acid, causing a contraction, on explosion, equal to 43.64 vols.

According to analysis, No. III. 14.29 vols. combustible gas consumed 83.34 vols. oxygen, and generated 50.67 vols. carbonic acid, causing a contraction of 46.96 vols.

If we take into consideration the composition of the gases evolved by the action of zinc upon iodide of ethyl,\* together with the proof given below, that the gas absorbed by sulphuric acid has exactly the composition and state of condensation of olefiant gas, there can scarcely be a doubt that the gaseous mixture remaining after the action of sulphuric acid, consists of ethyl and hydride of ethyl; and by forming two equations, in which the volume of the mixture and the amount of contraction produced by explosion with oxygen are taken into account, it is easy to ascertain their respective volumes, even independently of the quantity of oxygen consumed and carbonic acid generated, although these latter values may be used to control the result arrived at, by employing the amount of contraction only in the calculation. I prefer employing the observed contraction as the known quantity in the second equation, to either the volume of oxygen consumed or that of carbonic acid generated, because the number representing it is obtained from two readings which are least liable to slight sources of error, and contains within itself the results of the entire analysis, viz: the volume of combustible gas, the oxygen consumed, and the carbonic acid generated.

It will be obvious, on inspecting its formula, that 1 vol. of ethyl requires for its combustion 6.5 vols. oxygen, and generates 4 vols. carbonic acid; and as the contraction, which occurs on explosion, is equal to the volume of the combustible gas + the volume of oxygen consumed — the amount of carbonic acid generated, it is evident that the gas in question will cause a contraction equal to 3.5 times its own volume; and for similar reasons—since hydride of ethyl consumes 3.5 times its own volume of oxygen, and generates twice its volume of carbonic acid—this gas must produce a contraction, on explosion, equal to 2.5 times its own volume.

\* Chem. Soc. Qu. J. II, 277.

If then, we represent the volume of this combustible mixture by  $A$ , the contraction produced by explosion with excess of oxygen by  $B$ , and the volumes of ethyl and hydride of ethyl respectively by  $x$  and  $y$ , we have the following equations:

$$x + y = A$$

$$\frac{7}{2}x + \frac{5}{2}y = B$$

from which the values of  $x$  and  $y$  are found to be

$$x = \frac{2B - 5A}{2}$$

$$y = \frac{7A - 2B}{2}$$

and by substituting the numbers found in analyses Nos. II. and III., for  $A$  and  $B$  we have

	II.	III.
$x$	10.54	11.23
$y$	2.70	3.06
	13.24	14.29

Hence, the gas unabsorbed by fuming sulphuric acid contains in 100 parts:

	II.	III.	MEAN.
Ethyl	79.61	78.59	79.10
Hydride of Ethyl	20.39	21.41	20.90
	100.00	100.00	100.00

In order to ascertain the composition and state of condensation of the gaseous body absorbed by fuming sulphuric acid, the original gas, before being exposed to the action of that acid, was exploded with atmospheric air and excess of oxygen. The following results were obtained:

IV.					
	Observed vol.	Temp.	Difference of mercury level.	Barom <sup>r</sup> .	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Vol. of gas used (moist).	96.3	9.4°C.	575.9 <sup>mm</sup>	747.5 <sup>mm</sup>	15.16
Vol. after admission of air and O (moist)		9.5° „	68.9 „	746.7 „	381.83
Vol. after explosion (moist).	549.2	9.7° „	105.4 „	746.7 „	335.34
Vol. after absorption of CO <sub>2</sub> (dry).		7.4° „	158.1 „	752.1 „	284.59

According to this analysis, 15·16 vols. of the gas consumed 82·08 vols. oxygen, and generated 50·75 vols. carbonic acid; but analysis No. I. shows that this quantity of gas contains 12·99 vols. of the mixture of ethyl and hydride of ethyl, which, according to the mean of analyses Nos. II. and III., would consume 75·99 vols. oxygen, and generate 46·24 vols. carbonic acid; thus leaving 6·09 vols. oxygen, and 4·51 vols. carbonic acid as the oxygen consumed and carbonic acid generated by the 2·17 vols. of the gas absorbable by sulphuric acid, 1 vol. of which must, therefore, have consumed 2·81 vols. O and generated 2·08 vols. carbonic acid.

Vol. of comb. gas.	O consumed.	CO <sub>2</sub> generated.
2·17	6·09	4·51
1 :	2·81 :	2·08

When we reflect that in this experiment all the errors of observation are concentrated upon a very small proportion of the gas submitted to analysis, the numbers obtained agree sufficiently with those yielded by the combustion of olefiant gas, to allow safely of the conclusion that the body absorbed by sulphuric acid is the gas in question; for 1 vol. of olefiant gas consumes 3 vols. oxygen and generates 2 vols. carbonic acid.

The composition of the gases evolved by the action of light upon iodide of ethyl, in presence of mercury, may therefore, according to the mean of the above analyses, be thus centessimally expressed:

Ethyl	.	.	.	.	.	67·76
Hydride of ethyl	.	.	.	.	.	17·90
Olefiant gas	.	.	.	.	.	14·34
						<hr/> 100·00

The theoretical specific gravity of a gaseous mixture of this composition agrees closely with that found by experiment, as shown by the following calculation:

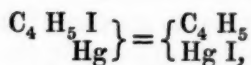
$$\begin{array}{rcl}
 \text{C}_4 \text{H}_5 & = & 67\cdot76 \times 2\cdot00390 = 135\cdot7843 \\
 \text{C}_4 \text{H}_5, \text{H} & = & 17\cdot90 \times 1\cdot03652 = 18\cdot5537 \\
 \text{C}_4 \text{H}_4 & = & 14\cdot34 \times 0\cdot96742 = 13\cdot8728 \\
 \hline
 & & 100\cdot00 \qquad \qquad 168\cdot2108 \\
 & & \hline
 & & 100 \qquad \qquad \qquad = 1\cdot682108
 \end{array}$$

Specific gravity, as found by experiment . . . . 1·7159

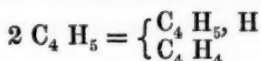
Hence the decomposition suffered by iodide of ethyl, under the



influence of light, and in presence of mercury, is expressed by the following equation :



a small portion of the liberated ethyl being at the same time transformed into equal volumes of olefiant gas and hydride of ethyl :



The slight deficiency of olefiant gas, as exhibited by the analyses, may very probably be owing to the different solubility of the two gases in the sulphuretted water which was used as the confining medium, during their purification from the vapour of iodide of ethyl.

The action of light upon iodide of hydrogen and iodide of ethyl is therefore perfectly analogous ; in the one case we have the simple radical hydrogen eliminated, and in the other the compound radical ethyl. This reaction is also perfectly parallel with that produced by the action of heat upon iodide of ethyl in presence of zinc,\* except that, in this last decomposition, a considerably larger portion of the ethyl is transformed into hydride of ethyl and olefiant gas. The proportion of ethyl which undergoes this transformation in the two reactions just mentioned, and in one which I describe below, is worthy of remark : it is best seen from the composition of the gases left after the action of fuming sulphuric acid.

I. Gases evolved by action of zinc upon iodide of ethyl :

$$\begin{array}{rcl} \text{C}_4 \text{H}_5 & : & \text{C}_4 \text{H}_5 \text{H} = 50.03 & : & 25.79 \\ & & = 1.94 & : & 1.00 \end{array}$$

II. Gases evolved by action of light upon iodide of ethyl in presence of mercury :

$$\begin{array}{rcl} \text{C}_4 \text{H}_5 & : & \text{C}_4 \text{H}_5 \text{H} = 79.10 & : & 20.90 \\ & & = 3.78 & : & 1.00 \end{array}$$

III. Gases evolved by action of light upon iodide of ethyl in presence of mercury and water :

$$\begin{array}{rcl} \text{C}_4 \text{H}_5 & : & \text{C}_4 \text{H}_5 \text{H} = 11.535 & : & 3.055 \\ & & = 3.78 & : & 1.00 \end{array}$$

As the hydride of ethyl occupies exactly the same volume as the ethyl from which it is derived, it is evident that, in the first reaction,

\* Chem. Soc. Qu. J. II, 281.

exactly  $\frac{1}{3}$ rd, and in the second and third very nearly  $\frac{1}{3}$ th of the ethyl evolved undergoes this transformation.

It was not without interest to ascertain if the action of light upon iodide of ethyl is modified in any way by the presence of water, as was the case in the corresponding reaction with zinc, where the whole of the ethyl was converted into hydride of ethyl by the assumption of an atom of hydrogen from the water, whilst the oxygen of the latter united with zinc to form an oxyiodide.

ACTION OF LIGHT UPON IODIDE OF ETHYL IN PRESENCE OF  
MERCURY AND WATER.

Iodide of ethyl, mixed with about twice its volume of distilled water, was exposed, as before, to the direct solar rays: precisely the same phenomena were observed as when the iodide alone was used, although the production of gas seemed to take place more rapidly when water was present. The gases were collected, purified from iodide of ethyl vapour, and examined by the methods described above.

A determination of the specific gravity of the gas gave the following numbers:

Temperature of room . . . . .	20.3°C.
Height of barometer . . . . .	765.9 <sup>mm</sup>
Height of internal column of mercury . . . . .	12.9 „
Weight of flask and gas . . . . .	33.5639 grms.
Temperature in balance-case . . . . .	21.3°C.
Weight of flask filled with dry air . . . . .	33.4492 grms.
Temperature in balance-case . . . . .	21.2°C.
Capacity of flask . . . . .	140.65 cbe.

From which the specific gravity was estimated at 1.6944.

The eudiometrical analysis gave the following readings:

In absorption eudiometer.

I.

	Observed vol.	Temp.	Difference of mercury level.	Barom <sup>r</sup> . at 0° C. and 1 <sup>m</sup> pressure.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Volume of gas used } (dry).	181.1	20.3°C.	55. <sup>mm</sup>	765.9 <sup>mm</sup>	128.17
Vol. after action of } SO <sub>3</sub> (dry).	153.3	18.7° „	3.4 „	764.9 „	109.25
Vol. after admission } of alcohol.	0.0	—	—	—	0.00

## In combustion eudiometer.

## II.

	Observed vol.	Temp.	Difference of mercury level.	Barom <sup>r</sup> .	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Vol. of gas used } (moist)	96.0	19.2°C.	585.7 <sup>mm</sup>	764.9 <sup>mm</sup>	14.59
Vol. after admission } of air (moist).	516.5	19.4° „	144.8 „	764.7 „	290.87
Vol. after admission } of O (moist).	605.2	19.7° „	64.9 „	764.5 „	385.24
Vol. after explosion } (moist).	562.3	20.0° „	103.1 „	764.2 „	337.23
Vol. after absorption } of CO <sub>2</sub> (dry).	503.8	18.8° „	156.4 „	765.5 „	287.08
Vol. after admission } of H (dry).	689.7	21.1° „	2.6 „	762.9 „	486.75
Vol. after explosion } (moist).	518.1	21.6° „	153.3 „	762.5 „	283.27

From analysis No. I. it follows that the gas contains in 100 parts :

Gas absorbable by SO <sub>3</sub>	.	.	.	14.76
Gas unabsorbable by SO <sub>3</sub>	.	.	.	85.24
				<hr/> 100.00

And its perfect absorption by alcohol proves the absence of hydrogen, hydride of methyl, and nitrogen.

Analysis No. II. shows that 14.59 vols. of the gas left intact by fuming sulphuric acid consumed 83.57 vols. oxygen, and generated 50.15 vols. carbonic acid, causing a contraction, on explosion, equal to 48.01 vols.

From a simple inspection of these figures, it is evident that we have the same gaseous mixture to deal with as in the previous decomposition of iodide of ethyl without the presence of water, and, on applying the formulæ given above, we obtain the following values for  $x$  and  $y$  :

$$\begin{array}{rcl}
 x & = & 11.535 \\
 y & = & 3.055 \\
 & & \hline
 & & 14.590
 \end{array}$$

Hence the gas, before being acted upon by fuming sulphuric acid, consisted of :

Ethyl	.	.	.	.	.	.	67.39
Hydride of ethyl	.	.	.	.	.	.	17.85
Olefiant gas	.	.	.	.	.	.	14.76
							<hr/>
							100.00

The determination of its specific gravity, given above, also confirms this result, as is seen from the annexed calculation :

$$\begin{array}{rcl}
 \text{C}_4 \text{H}_5 & = & 67.39 \times 2.00390 = 135.0430 \\
 \text{C}_4 \text{H}_5 \text{H} & = & 17.85 \times 1.03652 = 18.5019 \\
 \text{C}_4 \text{H}_4 & = & 14.76 \times 0.96742 = 14.2791 \\
 & & \hline
 & & 167.8240 \\
 & & \hline
 & & 100
 \end{array} = 1.67824$$

Specific gravity as found by experiment . . 1.6944

The presence of water consequently exerts no modifying influence over the decomposition of iodide of ethyl by light, the products formed with and without the presence of water being identical both in composition and relative proportion. The transformation of ethyl into hydride of ethyl, when its iodide is decomposed by zinc in contact with water, is therefore probably owing to the high affinity of zinc for oxygen, rather than that of ethyl for hydrogen, although both affinities no doubt take part in causing the resolution of water into its elements.

The above decomposition of iodide of ethyl by light, depending, as it does, directly upon the chemical rays, furnishes us with the materials for the construction of an actinometer of considerable delicacy, since the volumes of gas (corrected for tension of iodide of ethyl vapour, &c.) evolved in equal times, would give us the relative quantities of the actinic influence falling upon a given surface during these times; thus daily, or even hourly readings of the instrument could be made during the time the sun is above the horizon, and a register of the actinic influence, in different localities, be kept with as much ease as registers of the atmospheric pressure and temperature. I have not ascertained how small a quantity of light can determine the decomposition of the iodide; but very weak diffused daylight, as for instance, on a very cloudy or foggy day, is sufficient to produce a very considerable disengagement of gas, the volume of which could of course be read off at stated times with the greatest facility, and without even interrupting the action of the instrument.

I have also studied the action of solar light upon the iodide of

methyl, as well as upon the iodides of ethyl and methyl in contact with the various metals, which has led to the discovery of an entirely new series of organo-metallic radicals, possessed of very remarkable and interesting properties; the results of these researches I hope shortly to have the honour of laying before the Royal Society.

The foregoing experiments form, I think, another link in the chain of evidence which establishes the homology of hydrogen with the radicals of the series to which ethyl and methyl belong, and the simplicity of the decomposition by which the ethyl is here separated from the iodine by the action of an imponderable agent, seems, to some extent, to disarm of their force several of the arguments lately employed with so much ingenuity by Dr. Hofmann\* against the formulæ which I proposed for these bodies. In order to decide upon the truth or falsity of the views entertained by MM. Laurent and Gerhardt respecting these compounds, according to whom their formulæ ought to be doubled, and the bodies themselves classed amongst the members of the marsh-gas series, Dr. Hofmann undertook the examination of the products resulting from the action of heat upon valeric acid, in the hope of obtaining the hitherto unknown member of the marsh-gas family, represented by the formula  $C_8 H_{10}$ , which, if identical with the gas evolved by the action of zinc upon iodide of ethyl, would render necessary the doubling of the formula of the latter gas; whereas, if the body  $C_8 H_{10}$  were not identical with the so-called ethyl, it would afford strong evidence in favour of my formula being the correct one. Unfortunately, Dr. Hofmann did not succeed in obtaining this body, and thus the question was left in the same condition as before.

In a former memoir† I have described two separate series of carbo-hydrogens isomeric with each other, the one consisting of the bodies which I consider as the alcohol radicals, and the other containing the members of the marsh-gas family, which I regard, from the mode in which they are formed, as the hydrides of these radicals; thus:

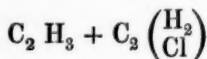
Radicals.			Marsh-gas family, or hydrides.		
Methyl	C <sub>2</sub>	H <sub>3</sub>	{ Hydride of methyl (light carburetted hydrogen) } C <sub>2</sub> H <sub>3</sub> . H		
Ethyl	C <sub>4</sub>	H <sub>5</sub>	ethyl	.	C <sub>4</sub> H <sub>5</sub> . H
Propyl	C <sub>6</sub>	H <sub>7</sub>	propyl	.	C <sub>6</sub> H <sub>7</sub> . H
Butyl	C <sub>8</sub>	H <sub>9</sub>	butyl	.	C <sub>8</sub> H <sub>9</sub> . H
Amyl	C <sub>10</sub>	H <sub>11</sub>	amyl	.	C <sub>10</sub> H <sub>11</sub> . H
&c.			&c.		

\* Chem. Soc. Qu. J. III, 121.

† Ib. III, 50.

It is obvious, on inspecting the above columns, that the members on the left hand are isomeric with those on the line next below them in the right hand column. Now, two of these bodies, which are represented as isomeric in the table just given, have been already obtained; viz., methyl ( $C_2 H_3$ ) by the electrolysis of acetic acid\* and the decomposition of iodide of methyl by zinc;† and hydride of ethyl by the decomposition of cyanide of ethyl (not perfectly anhydrous) by potassium,‡ and by the action of zinc upon iodide of ethyl in presence of water,§ and it is therefore only requisite to establish the *identity* or *isomerism* of these bodies, in order to test the correctness of the two views which have been proposed. As both the bodies in question are gaseous at ordinary temperatures, and do not change this condition under a pressure of 20 atmospheres, it is evident that their physical properties cannot assist us in deciding the question; besides, even assuming them to be isomeric, I should not expect any difference either in their boiling points or specific gravities. Under these circumstances, chlorine appeared to be the agent best suited to determine the point at issue; because, although we could only expect to obtain substitution products, yet the nature of these products must at once give us the key to the atomic weight of the bodies before us; for if we found  $\frac{1}{6}$ th of the hydrogen substituted by chlorine, then, according to the usual interpretation of this phenomenon, we must assume the simplest atom to contain 6 atoms of hydrogen, and if, under similar circumstances,  $\frac{1}{3}$ rd of the hydrogen were substituted, we should have an equal right for judging the simple atom to contain only 3 equivalents of hydrogen.

The action of chlorine upon the so-called hydride of ethyl in diffused daylight has already been studied by Kolbe and myself,|| and we find that 1 vol. of hydride of ethyl, and 1 vol. of chlorine give 1 vol. hydrochloric acid and 1 vol. of a gas having the formula  $C_4 H_5 Cl$ , but which is only isomeric, and not identical, with chloride of ethyl; we proposed for it the formula:



which represents 1 atom of methyl conjugated with another atom of the same group in which 1 atom of hydrogen has been replaced by chlorine. From considerations deduced from the production of hydride of ethyl, I now regard this chlorine compound as  $C_4 \begin{array}{c} H_4 \\ Cl \end{array} H$ ,

\* Chem. Soc. Qu. J. II, 173.

† Ibid. II, 267.

‡ Chem. Soc. Qu. J. I, 60.

§ Ibid. II, 288.

|| Chem. Soc. Qu. J. I, 66.



hydride of ethyl in which 1 atom of hydrogen in the group  $C_4 H_6$  has been replaced by chlorine; and this view explains why the body in question is isomeric and not identical, with chloride of ethyl. However, in whatever way this compound is viewed, it is evident that  $\frac{1}{6}$ th of its hydrogen has been replaced by chlorine.

It was now necessary to study the action of chlorine upon the body to which I assign the formula  $C_2 H_3$ . As there are difficulties which I have not yet been able to overcome, in the way of procuring this body *pure* by the action of zinc upon iodide of methyl, I employed Kolbe's method by the electrolysis of acetic acid. The apparatus used was the same as that described by that chemist in his memoir, except that the gases evolved from the positive pole were allowed to stream through a long series of bulbs filled with a solution of caustic potash, by which every trace of carbonic acid was removed; behind this bulbous tube were fixed three Liebig's potash apparatus, the first filled with fuming sulphuric acid, the second with solution of potash, and the third with concentrated sulphuric acid, the last being employed to dry the gas perfectly before it passed into the tubes\* which were destined afterwards to be used for the experiments: the system of tubes terminated in a delivery-tube leading to the mercury-trough. As soon as the gas evolved in this last was perfectly absorbed by recently-boiled alcohol, a specimen was collected for analysis, and the tubes now filled with the pure gas were hermetically sealed at one end, and the caoutchouc connector at the other being securely tied, cut, and covered with melted wax, they were taken asunder and reserved for the subsequent experiments.

The specimen of the gas collected as just described, was exploded with excess of oxygen, and gave the following numbers.

	Observed vol.	Temp.	Difference of mercury level.	Barom <sup>r</sup> .	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Vol. of gas used (moist).	100.0	16.5°C.	576.4 <sup>mm</sup>	752.5 <sup>mm</sup>	15.28
Vol. after admission of O (moist).	323.3	17.0° „	330.7 „	751.8 „	123.77
Vol. after explosion (moist).	266.4	17.2° „	390.5 „	751.6 „	86.83
Vol. after absorption of CO <sub>2</sub> (dry).	206.2	16.4° „	455.8 „	749.3 „	57.09
Vol. after admission of H (dry).	521.6	17.1° „	136.0 „	748.9 „	300.83
Vol. after explosion (moist).	332.5	16.8° „	320.6 „	749.0 „	129.73

\* The form of these tubes is shown in a figure given in this Journ. Vol. I, p. 6 Fig. I, e-f.

The proportion between the volumes of combustible gas, oxygen consumed, and carbonic acid generated, may therefore be thus stated :

Vol. of comb. gas.	O consumed.	CO <sub>2</sub> generated.
15.28	51.41	29.74
1	3.36	1.95

The numbers required theoretically for methyl are :

1	3.5	2
---	-----	---

A number of tubes, some of the same, and others of exactly double the capacity of those containing methyl, were then prepared and filled with dry chlorine by displacement; they were afterwards sealed at one extremity, the caoutchouc connecter at the opposite end being securely tied and covered with melted wax.

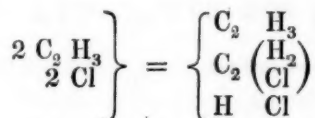
#### ACTION OF CHLORINE UPON AN EQUAL VOLUME OF METHYL.

Two tubes of exactly the same capacity, the one containing chlorine, and the other methyl, were quickly connected together by inserting their narrow necks into a strong caoutchouc connecter, and securing them by silk ligatures; they were placed in perfect darkness for 18 hours, to allow the gases to become thoroughly mixed. On being afterwards exposed to diffused daylight, the colour of the chlorine rapidly disappeared, showing that combination ensued. After being allowed to stand in the light for several hours, the tubes were hermetically sealed, and their contents submitted to eudiometrical examination. On breaking off their extremities under mercury, it was evident that no contraction of volume had taken place; but the dense fumes caused by allowing a few bubbles of the gas to escape into the atmosphere, proved that hydrochloric acid was one of the products of the reaction, and that the two gases had not simply united to form chloride of methyl. The contents of both tubes were transferred into a eudiometer, and the volume of hydrochloric acid was estimated by absorption, first with a ball of aqueous tribasic phosphate of soda, and afterwards with a bullet of fused potash, which last also dried the residual gas perfectly.

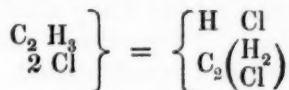
The following numbers were read off:

	Observed vol.	Temp.	Difference of mercury level.	Barom <sup>r</sup> .	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Vol. of gas used (dry).	145.6	19.2°C.	10.0 <sup>mm</sup>	769.2 <sup>mm</sup>	103.27
Vol. after absorption of HCl (dry).	81.2	18.4° „	80.6 „	766.1 „	52.14

Thus, it appears that the products of the action of 1 vol. of chlorine on 1 vol. of methyl, are 1 vol. of hydrochloric acid and 1 vol. of another gas, which must necessarily have the empirical formula  $C_4 H_5 Cl$ , expressing 4 vols. This is exactly the result obtained by Kolbe and myself in acting with an equal volume of chlorine upon the hydride of ethyl obtained by the action of potassium upon cyanide of ethyl, and thus, up to the present point, the experiments seem to prove the *identity* of the two bodies—the so-called methyl, and the hydride of ethyl. But these experiments admit also of a different interpretation; for if we assume that the chlorine acted upon only half of the methyl employed, then the following equation would express the reaction:



2 vols. of chlorine acting upon 1 vol. of methyl produce 1 vol. hydrochloric acid, and 1 vol. of chlormethyl  $C_2 \left( \begin{matrix} H_2 \\ Cl \end{matrix} \right)$  which last remains mixed with the excess of methyl employed. It would be very difficult to determine directly whether the gas in question is a mixture or a single gas; or, in other words, whether methyl and hydride of ethyl yield *identical* or *isomeric* results when acted upon by an equal volume of chlorine; but this question can be easily decided by employing an additional volume of chlorine, by which, if the view of the reaction just stated be correct, the excess of methyl will also undergo the process of substitution, and the result should be 1 vol. of methyl *gas*, in which 1 atom of hydrogen has been replaced by chlorine  $\left\{ C_2 \left( \begin{matrix} H_2 \\ Cl \end{matrix} \right) \right\}$  and 2 vols. hydrochloric acid.



#### ACTION OF 2 VOLUMES OF CHLORINE UPON 1 VOL. OF METHYL.

Two tubes were connected together, the one having a capacity exactly twice as great as the other, the first being filled with dry chlorine, and the last with methyl; as in the former experiment, they were excluded from light for 18 hours, to secure the perfect mixture of the two gases, before allowing the chlorine to act. On afterwards bringing the tubes into diffused daylight, their interior became

bedewed with minute drops of an ethereal fluid, which, however, again disappeared after the lapse of a few minutes, and on opening the tubes under mercury, after the action was completed, no contraction of volume was perceived to have taken place. The contents being transferred to a eudiometer, the hydrochloric acid was determined as before.

The following numbers were obtained :

	Observed vol.	Temp.	Difference of mercury level.	Barom <sup>r</sup> .	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Vol. of gas used (dry).	157·3	18·3°C.	9·7 <sup>mm</sup>	767·5 <sup>mm</sup>	111·71
Vol. after absorption of H Cl (dry).	60·3	18·5° „	97·5 „	773·8 „	38·19
Vol. of residual gas.	38·19		Vol. of H Cl.		
	1	:	73·52		
			1·92		

Hence it follows that 1 vol. methyl and 2 vols. chlorine, yield 2 vols. hydrochloric acid, and 1 vol. of another gas, which must have the formula  $C_2 H_2 Cl$ , expressive of 2 vols. of vapour; but this is the formula and state of condensation of the radical methyl in which 1 atom of hydrogen has been replaced by chlorine; and the action of 2 vols. of chlorine upon 1 vol. of methyl is therefore correctly expressed in the equation given above.

As a final proof of the correctness of this mode of interpretation, and of the *isomerism* of methyl and hydride of ethyl, it remained only to try the action of 2 vols. of chlorine upon 1 vol. of the latter body. For this purpose, hydride of ethyl was procured by the action of zinc upon iodide of ethyl in presence of water, a process which, as I have shown,\* yields that gas in a state of absolute purity. One volume of this gas, perfectly dried, being mixed, as before described, with 2 vols. of chlorine, and the intimate mixture then exposed to diffused daylight, combination rapidly ensued, and the walls of the tubes became wetted with a considerable quantity of an oleaginous fluid, which did not disappear or diminish even after the lapse of several weeks, during which time the tubes had been hermetically sealed. On breaking off their ends under mercury, a considerable contraction was observed to have taken place, the residual gas not occupying more than  $\frac{2}{3}$  rds of the original volume. It was transferred into a eudiometer, and on being treated with a ball of phosphate of

\* Chem. Soc. Q. J. II, 291.

soda, was so nearly absorbed, that the very small volume of gas remaining after its action could not be determined. This experiment allows us to conclude that 2 vols. of chlorine with 1 vol. of hydride of ethyl yield 2 vols. hydrochloric acid, and a liquid which, from the volumes of the gases taking part in its formation, has probably the formula  $C_4 H_4 Cl_2$  and the same percentage composition as the oil of olefiant gas ( $C_4 H_3 Cl + H Cl$ ); but whether the oily liquid produced in the above reaction be identical with this body, I have not been able to determine, as the quantity of the gaseous hydride of ethyl which would be required to form a sufficient amount of liquid to be subsequently purified for analysis would be very great.

The results of these experiments on the action of chlorine upon methyl and hydride of methyl do not agree quite so nearly with theoretical calculations as I could wish, owing to a slight amount of impurity contained in the methyl, as indicated by the analysis of that gas, the quantity of oxygen consumed being rather too far below the theoretical volume to be accounted for by possible errors of observation. I have been at great pains to remove this foreign body, but without success: Dr. Kolbe found the same difficulty when he first investigated this gas, and attributed the smaller quantity of oxygen consumed to the presence of a trace of oxide of methyl. As the impurity can only be present, however, in very minute quantity, it could scarcely have any material influence upon the results of the experiments, and I therefore think they allow us safely to conclude,

1st. That there exist two series of hydrocarbons of the form  $C_n H_{n+1}$ , the members of the one series being isomeric with those of the other, and

2nd. That the formula of the gaseous hydrocarbon obtained by the electrolysis of acetic acid is  $C_2 H_3$ , its atom being represented by 2 volumes of vapour; whilst the gas procured by the action of potassium upon cyanide of ethyl (not anhydrous), and by the action of zinc upon iodide of ethyl in presence of water, has the formula  $C_4 H_6$ , its atom being represented by 4 volumes of vapour.

As soon as I have succeeded in procuring pure methyl by the action of zinc upon its iodide, I intend to repeat these experiments and make them more complete.

Although Dr. Hofmann regards the decision of the above question as sufficient to establish the correctness of one or the other of the views which have been advanced respecting these radicals, on the one hand by MM. Laurent and Gerhardt, and on the other by Dr. Kolbe and myself, yet I do not deem it superfluous to offer a few remarks upon the arguments which Dr. Hofmann has used with so much

skill against the formulæ we have proposed for the bodies in question, especially as several of these arguments appear, at first sight, very conclusive.

The objections which this chemist has made to these bodies being considered as radicals may be thus expressed :

1st. The new radicals do not combine directly with the metalloids ; none of them have been found capable of reproducing a methyl-, ethyl-, or amyl-compound.

2nd. The volume of their vapours are different from that of all other known hydrocarbons.

3rd. The boiling-points of the compounds in question are in favour of their formulæ being doubled.

4th. The decomposition of the iodides of the alcohol-radicals by zinc is not *perfectly* analogous to that of hydriodic acid.

5th. The formulæ of these bodies require to be doubled to remove the discrepancy exhibited by the boiling-points of amylene, hydride of amyl, and amyl.

The first objection follows naturally, from the circumstance that, up to the time of the isolation of these bodies, we were only acquainted with one basic or electro-positive radical, in a separate form ; viz., cacodyl, which has unfortunately been looked upon by some chemists as a type of all other organic radicals, which they therefore expected to find endowed with similar powerful affinities. Such a partial view of the essential characters of a compound radical could not have been formed from a careful comparison of the varied properties of the simple radicals, which are undoubtedly the true types of their representatives in the organic world. A slight glance at the habits and affinities of these elementary bodies, exhibits to us the most widely-different powers of combination. Commencing with potassium and terminating with hydrogen, gold, platinum, iridium and nitrogen, we have a series of bodies which, although they all readily pass from one form of combination to another, when already combined, yet, when once isolated, exhibit as we ascend the scale an increasing reluctance to enter into union. Taking these reactions of the simple radicals then into consideration, it would be neither difficult nor visionary to predict that their organic representatives would be found possessed of as great a variety of disposition, and that we should have a corresponding series of bodies, commencing with cacodyl, zinc-methyl, zincethyl, stibethyl, &c., and terminating with the radicals of the alcohol family (the perfect representatives of hydrogen) exhibiting a similar decrease of combining power ; and, since the organic groups are so instable in their nature, and so liable to metamorphosis from



the slightest causes, that we are unable to expose them without utter destruction to the powerful influences which we can bring to bear upon an elementary body, it surely ought to be a matter of no great surprise, if the members of the least electro-positive extremity of the series should elude all our attempts to bring them again uninjured into combination. If nitrogen were decomposed at a red heat, by what means could we recombine that radical when once isolated? I am at present engaged in filling up the gap in the series between cacodyl and ethyl, and have been lately occupied in studying the properties of an organo-metallic radical, which seems to occupy a position about midway in the series, entering into direct combination with several of the metalloids, but with a degree of affinity immensely less than that exhibited by cacodyl or zinc-methyl.

Dr. Hofmann objects to the present formulæ of the radicals, in the second place, because their vapour-volumes are different from those of all other known carbo-hydrogens. In carefully considering this objection in all its bearings upon the subject, I have been quite unable to see its force, or to find in this difference of vapour-volume other than a very strong proof in favour of the bodies in question being the true radicals; for had their vapour-volumes corresponded with those of other carbo-hydrogens, it would, in my opinion, have afforded striking evidence of their being no radicals at all. Here, in order to seek for analogy, we must again return to the simple radical hydrogen, which presents such close relations to these organic groups, and in perfect harmony with them, has its atom represented by 2 volumes. The action of chlorine upon all the other hydrocarbons indicates that they contain an atom of hydrogen in combination with another group, and therefore their single atoms, like those of the hydrides of methyl, ethyl and amyl, are represented by 4 volumes of vapour, and they cannot possibly be brought forward as analogies for controlling the formulæ of the radicals themselves, with which the members of the series  $C_n H_n$  and  $C_n H_{n-6}$  are, by their properties and reactions, placed out of all connection.

But the objection which has the greatest apparent weight, and the one to which Dr. Hofmann evidently attaches the highest importance, is the 3rd; viz., "That the boiling-points of the compounds in question are in favour of their formulæ being doubled." The application of the beautiful and highly-interesting law of Professor Kopp to the controlling of the formulæ of an entirely new class of bodies, should be made with great caution; for although we can by its means unerringly predict the boiling-points of the members of the classes of compounds upon which that law was first founded, yet the extension

of the list of organic bodies has proved, beyond doubt, that the difference of  $18^{\circ}$  or  $19^{\circ}\text{C.}$  for each addition or subtraction of the elements  $\text{C}_2 \text{H}_2$ , by no means obtains when we apply it to other classes of compounds; in fact, these discrepancies might naturally be expected from a consideration of the effect which a difference in the specific and latent heat of different atoms must have upon the thermal properties of the compound; for it could not be expected that the boiling-point of water, for instance, should be raised through the same number of degrees by the addition of  $\text{C}_2 \text{H}_2$ , as that of other bodies having a much less specific and latent heat: hence we find that the difference in the boiling-point, produced by the addition of the elements  $\text{C}_2 \text{H}_2$  depends entirely upon the nature of the groups to which these elements are added. In the alcohols and the series of acids  $\text{C}_n \text{H}_n \text{O}_4$ , the elevation in the boiling-point produced by each addition of the elements  $\text{C}_2 \text{H}_2$  varies from  $16^{\circ}$  to  $21^{\circ}\text{C.}$  giving the mean number  $18.5^{\circ}\text{C.}$  and it was principally upon these series of bodies containing, in addition to water, two radicals—viz., ethyl, methyl, &c., and oxygen, that Kopp's law was founded; but if we examine bodies of more simple constitution, containing two radicals without water, we find the increase of the boiling-point produced by each addition of the elements  $\text{C}_2 \text{H}_2$  widely different from the above number. Thus, at the first step, we find between oxide of methyl and oxide of ethyl a difference of at least  $51^{\circ}\text{C.}$ ; for, according to Gay-Lussac and Dumas, oxide of ethyl boils at  $35.5^{\circ}\text{C.}$  whilst oxide of methyl is incondensable at  $-16^{\circ}\text{C.}$  The iodides of ethyl and methyl differ by about  $30^{\circ}\text{C.}$ , and the chlorides of ethyl and amyl by  $91^{\circ}\text{C.}$ , equivalent to  $30^{\circ}\text{C.}$  for each term of  $\text{C}_2 \text{H}_2$ , whilst the difference between chloride of ethyl and chloride of methyl is at least equally great, since the boiling-point of the former is  $11^{\circ}\text{C.}$  and the latter is still gaseous at  $-18^{\circ}\text{C.}$ : the sulphides also exhibit a difference varying from  $34^{\circ}$  to  $47^{\circ}\text{C.}$  for each equivalent of  $\text{C}_2 \text{H}_2$ . From these facts, it is easily perceived that the difference in the boiling-points produced by the addition or subtraction of the term  $\text{C}_2 \text{H}_2$  rapidly *increases* as the complexity of the compounds *decreases*; therefore we might reasonably expect that the radicals themselves, containing as they do only one group consisting of two elements, would exhibit a still greater difference, which is precisely what is found to be the case; amyl and valyl differ by  $47^{\circ}\text{C.}$  and ethyl and methyl will probably be found to differ to a still greater extent.

Although I am averse to drawing analogies from the habits of the hydrocarbon family  $\text{C}_n \text{H}_n$ , conceiving its members to have no connection with the groups in dispute, yet, since the *vapour-volume* of

these bodies has been brought forward as an argument in favour of doubling the formulæ of the radicals, I cannot refrain from referring to the *boiling-points* of these hydrocarbons  $C_n H_m$ , which, from the fact of their formulæ having already been once doubled, are not likely to undergo that process again by any discrepancies in this respect. The boiling-points of two of these—viz., butyrene and valerene, have been determined with tolerable exactness; the first was found by Faraday to boil at  $-17.8^\circ C.$ ; and the last by Balard at  $39^\circ C.$ , and by myself at  $35^\circ C.$ ; but as Balard's amylene was still mixed with small quantities of a body having a *higher* boiling-point, and the valerene obtained from iodide of amyl contained hydride of amyl, a compound boiling at a *lower* temperature, perhaps the mean  $37^\circ C.$  would be the most correct number. Here then we have two homologous bodies, differing from each other by the elements  $C_2 H_2$ , and approaching as near to valyl and amyl, in composition, as bodies belonging to a different family well could do—for valerene and butyrene differ only from amyl and valyl by containing one equivalent of hydrogen less—yet their boiling-points differ to the extent of  $54.8^\circ C.$ , which would require us to multiply their already doubled formulæ by 3 to reduce them to the standard of Kopp's law.

	Boiling-point.	Difference.
Amyl ( $C_{10} H_{11}$ ) . .	$155^\circ$ C. }	$47^\circ$ C.
Valyl ( $C_8 H_9$ ) . .	$108^\circ$ „ }	
Valerene ( $C_{10} H_{10}$ ) . .	$37^\circ$ „ }	$54.8^\circ$ „
Butyrene ( $C_8 H_8$ ) . .	$17.8^\circ$ „ }	

It does not therefore seem, that any argument in favour of doubling the formulæ of the radicals can be drawn from their boiling-points, but on the contrary, these boiling-points, taken in connection with those of their compounds, give additional evidence that the formulæ assigned to them are the correct ones.

A few words will suffice to remove the fourth objection, which is founded upon an experiment, in which Dr. Hofmann failed to produce the body zinc-hydrogen ( $Zn H$ ), by passing hydrochloric acid gas over metallic zinc, at an elevated temperature. The formation of zinc-hydrogen, under these circumstances, would have completed the analogy between the decomposition of chloride of hydrogen, and iodide of methyl; but as zinc is only very slowly acted upon by dry hydrochloric acid gas, even at a high temperature,\* the acid gas

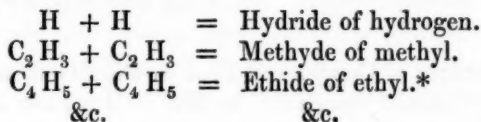
\* Chem. Soc. Qu. J. III, 47.

is always in excess, and consequently no other result than the one obtained could be looked for, any more than we could expect to preserve potassium in a stream of hot hydrochloric acid; for the series of bodies to which zinc-amyl, zinc-ethyl, and zinc-methyl belong, increase in the energy of their affinities as their atomic weights decrease; therefore we might predict, that zinc-hydrogen, if such a body exist, will be endowed with still more violent reactions than zinc-methyl. Now this last is instantaneously decomposed, with explosion, in hydrochloric acid gas; and therefore zinc-hydrogen, with perhaps still more powerful affinities, could not exist for a moment in a stream of that gas, or in other words, could never be formed in such an atmosphere. The action of iodide of methyl upon zinc-methyl is, however, but very slow even at an elevated temperature, to which circumstance we owe the presence of this body amongst the products of the decomposition of iodide of methyl by zinc; and if we ever obtain the body zinc-hydrogen, it must be by bringing nascent hydrogen, evolved from some nearly neutral body, in contact with zinc.

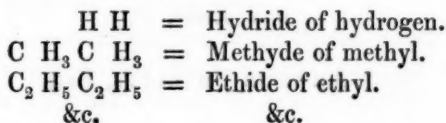
As the fifth objection, "that the formulæ of these bodies should be doubled to remove the discrepancies in the boiling-points of valerene, hydride of amyl and amyl," is not considered by Dr. Hofmann himself to have much weight, on account of the different vapour-volumes of the compounds precluding a proper comparison, I will only remark on this head, that the assimilation of an atom of hydrogen *with doubling* of the vapour-volume, and the same assimilation *without* increase of volume are widely different circumstances, from which we might naturally expect very different results as regards the boiling-points of the compounds thus produced; and, accordingly, when 2 vols. amyl vapour unite with 2 vols. hydrogen, to form 4 vols. hydride of amyl vapour, a depression of the boiling-point, from  $155^{\circ}$  to  $30^{\circ}$  C. =  $125^{\circ}$  C., takes place; but this cannot be regarded as extraordinary, unless it can be proved that the boiling-point of hydrogen is not  $125^{\circ}$  C. *below* that of hydride of amyl, for we are entitled to assume, *à priori*, that the boiling-point of such a body would be the mean of those of its constituents. When, however, 4 vols. of valerene vapour unite with 2 vols. of hydrogen, to form 2 vols. of amyl vapour, the 4 vols. of valerene are absorbed, as it were, into the two volumes of hydrogen, in other words, the 6 volumes are condensed to 2, and the consequence is that the boiling-point rises  $118^{\circ}$  C.

I have thus endeavoured to remove, *seriatim*, the objections which have been so ably and ingeniously made by Dr. Hofmann, to the

formulae proposed by Dr. Kolbe and myself, for the groups which we conceive to represent, when isolated, hydrogen—and in ethyl, methyl, and amyl compounds, the hydrogen contained in the parallel combinations of this element. That these groups do not belong to the marsh-gas family, as suggested by MM. Laurent and Gerhardt is, I think, proved by the action of chlorine upon methyl, as detailed above; whilst the production of, and action of chlorine upon the hydrides of these groups, clearly indicates that these hydrides form the so-called marsh-gas family: hence we should gain no single advantage by doubling the present formulae of the bodies in dispute, but on the contrary, we should then either have to assume the existence of a *third* class of isomeric compounds, of undefined constitution, or to double our present formula for hydrogen, and represent the simplest isolable molecule of that element by  $H + H$ , we should then have :



Or adopting the notation of Messrs. Laurent and Gerhardt, these formulae would be thus written :



which also shows that the views advocated by these chemists on the one hand, and Dr. Kolbe and myself on the other, exhibit no greater difference with respect to ethyl, methyl, &c., than they do with regard to hydrogen.

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\* This view of the rational constitution of these bodies was first suggested by Mr. Brodie, at a recent meeting of the Society.

Nov. 18, 1850.

RICHARD PHILLIPS, Esq., President, in the Chair.

The following presents were announced :

"The Improvement of Land, by Warping, Chemically considered by Thornton J. Herapath:" by the Author.

A donation of 199 volumes : by Mr. Griffin ; see page 412 ?

The following Papers were read :

"On the claims of the elementary substances, Silicon and Selenium, to be ranked among metals:" by Mr. Richard Adie, of Liverpool.

"On the existence of Copper and Lead in the Blood, and in other portions of the Animal Organism:" by Mr. J. Denham Smith.

XXVIII.—*On Potasso-gypsite, a double Sulphate of Potash and Lime.*

By J. ARTHUR PHILLIPS, Esq.

This substance is obtained as a secondary product in the manufacture of tartaric acid, and it will therefore be necessary to describe the circumstances under which it is produced, before detailing the properties and composition of the salt itself. Tartaric acid is, as is well known, made from the impure bitartrate of potash, which reaches this country in such a state as to yield, on an average, 72 per cent of crystallized acid.

The processes employed in the manufacture are briefly as follows : Into a large tun, capable of containing about three thousand gallons of water, are thrown from fourteen to fifteen hundred pounds of mashed chalk, which is agitated by means of a revolving arm, until the water and carbonate of lime have become perfectly incorporated, and a finely-divided mixture is obtained. When this is effected, about two tons of crude tartar are added, by means of an air-tight trap on the top of the vessel, and by the aid of heat, obtained by blowing



a jet of steam into the mixture, and constant agitation of the mass, the bitartrate of potash is made to transfer its free atom of acid to the lime, giving rise to the formation of insoluble tartrate of lime, soluble tartrate of potash, and the evolution of carbonic acid, which is conveyed away in leaden pipes to be employed in making bicarbonate of soda. As soon as the decomposition is completed, a sufficient portion of sulphate of lime, from a preceding operation, is added, for the purpose of decomposing the neutral tartrate of potash in solution. By the aid of heat and long-continued agitation, this is at length effected, and the vessel then contains a solution of sulphate of potash, together with the insoluble tartrate of lime, and small portions of the carbonate and sulphate of the same base, arising from the excess of these reagents originally employed. At this period of the manufacture, the agitation is arrested, the liquor is allowed to settle down, and the sulphate of potash drawn off from the tartrate of lime, which remains at the bottom of the tub. This is subsequently washed with three successive waters, which are added to the solution of sulphate of potash at first obtained. The insoluble tartrate of lime is afterwards decomposed by sulphuric acid, with formation of sulphate of lime and production of free tartaric acid, which is crystallized in the usual way, whilst the sulphate of potash, with which we are at present most interested, is conveyed away by large leaden gutters for evaporation.

At the manufactory of the Messrs. Pontifex, these liquors are first drawn into a large tubular steam-boiler, heated by the waste heat escaping from a set of coke-ovens. In this the potash solution is concentrated to about two thirds of its original volume, and then allowed to run into a series of large bacs containing coils of iron pipe, which are supplied with steam by means of the boiler in which the liquor is concentrated, and in these the evaporation is completed.

This boiler for concentration and supplying the steam-coils, gradually becomes coated by a hard deposit, in order to remove which, it becomes necessary, at intervals of about three months, to stop the ovens and run out the liquor. On these occasions, the cooling of the boiler and its contents is extremely slow, as the mass of brickwork which surrounds it renders the loss by radiation very inconsiderable. When it has sufficiently cooled, and the liquor has been run off, the greater part of its internal surface is found to be covered with transparent lamellar crystals, formed on a hard crystalline gangue. These are sparingly soluble in water, but are easily dissolved by dilute hydrochloric acid.

A qualitative analysis showed them to consist of lime, potash,

water, and sulphuric acid, and a quantitative examination gave the following results :

## FIRST ANALYSIS.

10.05	grs. gave	14.85	grs.	platinum-salt.
"	"	3.05	"	carbonate of lime.
9.28	"	0.51	"	water.
"	"	13.22	"	sulphate baryta.

## SECOND ANALYSIS.

10.23	grs. gave	15.10	grs.	platinum-salt.
"	"	3.10	"	carbonate of lime.
5.81	"	0.33	"	water.
"	"	8.21	"	sulphate baryta.

These numbers afford the following percentage results :

Potash	.	.	.	.	28.52	28.57
Lime	.	.	.	.	16.99	16.96
Sulphuric acid	.	.	.	.	48.94	48.55
Water	.	.	.	.	5.51	5.67
					<hr/>	<hr/>
					99.96	99.75

The above relations would lead to the empirical formula  $\text{KO}, \text{SO}_3 + \text{CaO}, \text{SO}_3 + \text{HO}$ , as may be seen by comparison with the following calculated amounts :

	No. of eqs.		Amounts.	Percentage.
Potash . . . .	1	=	47	28.67
Lime . . . .	1	=	28	17.02
Sulphuric acid . .	2	=	80	48.82
Water . . . .	1	=	9	5.49
				<hr/>
				100.00

Since, however, a variety of sulphate of lime, expressed by  $2(\text{CaO}, \text{SO}_3) + \text{HO}$ , has been found under nearly similar circumstances,\* it appears probable that, in reality, the water is divided between the sulphates of lime and potash, and that the crystals are composed of a double di-hydrated salt, of which the true formula is

\* Johnston, Phil. Mag. J. XIII. 325; also J. Pr. Chem. XVI, 100.

represented by  $2(\text{KO}, \text{SO}_3) + \text{HO} + 2(\text{CaO}, \text{SO}_3) + \text{HO}$ , and to this I propose to give the name of *Potasso-gypsite*.

Professor W. H. Miller, of Cambridge, who has had the kindness to examine the crystals of this substance, describes them as follows :

## PRISMATIC.

Symbols of the simple forms :

$a$  100,  $e$  101,  $u$  102,  $m$  110.

Angles between normals to the faces :

$e a$	. . .	46°	28'
$e e'$	. . .	87	4
$u a$	. . .	76	38
$u u'$	. . .	26	44
$m a$	. . .	52	58
$m m'$	. . .	74	4



The crystals exhibit faint indications of cleavage parallel to a plane perpendicular to the faces  $a$ ,  $m$ .

The faces  $a$ , are striated parallel to their intersections with the faces  $m$ . The crystals are very thin in a direction perpendicular to the faces  $a$ .

The optic axes lie in a plane perpendicular to the faces  $a$ ,  $m$ . Seen in air, through the faces  $a$ , they appear to make angles of  $22^\circ 45'$ , with a normal to  $a$ , and an angle of  $45^\circ 30'$  with each other.

The crystalline gangue, on which the regular crystals are formed, was found, on analysis, to yield the following results :

## FIRST ANALYSIS.

28.95	grs. gave	0.23	grs. of	silica.
"	"	12.49	"	carbonate of lime.
"	"	1.19	"	phosphate of magnesia.
37.86	"	2.95	"	carbonic acid.
"	"	41.96	"	sulphate of baryta.
"	"	39.63	"	platinum-salt.
"	"	0.31	"	chloride of sodium.
24.12	"	0.30	"	oxide of iron.
"	"	0.18	"	alumina.
75.83	"	0.58	"	phosphate of magnesia.

## SECOND ANALYSIS.

26.23	grs. gave	0.25	grs. of	silica.
"	"	0.28	"	oxide of iron.
"	"	0.21	"	alumina.
25.57	"	0.87	"	phosphate of magnesia.
24.12	"	1.90	"	carbonic acid.
"	"	26.20	"	platinum-salt.
"	"	0.30	"	chloride of sodium.
"	"	9.34	"	sulphate of baryta.
"	"	0.17	"	phosphate of magnesia.

	I.	II.
Potash . . . .	20.18	20.93
Soda . . . .	0.43	0.61
Lime . . . .	24.16	"
Magnesia . . . .	1.50	1.24
Alumina . . . .	0.74	0.80
Oxide of iron . . . .	1.24	1.06
Silicic acid . . . .	0.79	0.80
Sulphuric acid . . . .	38.08	38.66
Phosphoric acid . . . .	0.49	0.42
Carbonic acid . . . .	7.79	7.87
Water . . . .	4.31	"
Organic matter . . . .	traces	traces

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 99.71

These numbers indicate that the uncrystallized portion of the deposit consists of the same substances as the crystals themselves; and if, in the first analysis, we so arrange them as to form the double sulphate above-described, the following percentages will be obtained:

	I.	II.
New salt . . . .	64.76	
Sulphate of lime . . . .	11.57	
Carbonate of lime . . . .	14.06	
Phosphate of lime . . . .	1.06	
Carbonate of magnesia . . . .	3.10	
Silicate of potash . . . .	2.42	
Oxide of iron . . . .	1.24	
Alumina . . . .	0.74	
Water . . . .	0.76	
Organic matter . . . .	traces	

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 99.71

In the analysis of the crystals of the pure salt, the water was estimated by heating to redness, in a platinum crucible, a portion of the substance which had been kept until it ceased to lose weight under the receiver of the air-pump, in which was placed a dish of strong sulphuric acid. The same portion of substance was then dissolved in dilute hydrochloric acid, and the sulphuric acid thrown down as sulphate of baryta by chloride of barium in the usual way. A second quantity of substance was then taken, and after dissolving it in dilute hydrochloric acid, and adding ammonia, the lime was precipitated in the form of oxalate, and weighed as carbonate. The filtrate from the oxalate of lime was then evaporated to dryness, and the residue heated to redness to expel the ammoniacal salts. A slight excess of hydrochloric acid was afterwards added, and the potash estimated as platino-chloride of potassium.

In the investigation of the uncrystallized deposit, the ordinary routine of chemical analysis was employed, the phosphoric acid being estimated by the method of Fresenius, and the alkalis separated from the alkaline earths by the use of hydrate of baryta.

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XXIX.—*On Chlorophosphuret of Nitrogen, and its Products of Decomposition.*

PART II.

By J. H. GLADSTONE, PH.D., F.C.S.

In my former Paper upon Chlorophosphuret of Nitrogen,\* it was stated that the decomposition which the solutions of that substance in alcohol and ether spontaneously undergo, would be reserved for after-consideration. I now return to that part of the inquiry.

It was early observed, that when the white mass produced by the action of ammoniacal gas on pentachloride of phosphorus, was washed with ether, to separate the chlorophosphuret of nitrogen, and the solution suffered to evaporate, other substances beside the crystalline body in question made their appearance. The chlorophosphuret was coloured pink or red, and smelt strongly of hydrochloric acid; and, upon the addition of water, it was evident that some body possessing oily properties was also present; whilst the aqueous solution reacted very acid, and upon evaporation after the hydrochloric acid had been driven off, left a semi-crystalline mass,

\* Chem. Soc. Qu. J. X. 135.

very soluble in water, but insoluble, or nearly so, in alcohol. This was powerfully acid to test-paper, was capable of being neutralized by potash, and a slightly acid solution gave flocculent white precipitates with nitrate of silver and chloride of calcium, requiring considerable excess of nitric acid to redissolve them.

In fact, ether was found capable of effecting a gradual, but complete transformation of chlorophosphuret of nitrogen into hydrochloric acid, the new acid just mentioned, and a varying amount of yellowish liquid, immiscible in water, having an aromatic odour. If the ethereal solution be heated, the change is immediately brought about, the oily liquid being produced in such quantity as to render the solution turbid.

The action of alcohol is equally destructive; but hydrochloric acid and the oily body are the sole products. If some crystals of chlorophosphuret of nitrogen be placed in a small quantity of alcohol, quite inadequate to dissolve them, they will be found in a few days to have disappeared, the oily body into which they have been transformed being taken up by the alcohol.

#### DEUTAZOPHOSPHORIC ACID.

The acid produced from chlorophosphuret of nitrogen, under the influence of ether, crystallizes in feathery crystals, or groups of microscopic spiculæ. That the substance is free from ammonia is evident from the fact that it does not yield that gas when boiled with baryta-water or weak potash; and as the neutralized solution gives no precipitate when mixed with a metallic salt, it cannot contain either phosphoric or azophosphoric acid.

The acid crystals, dried *in vacuo* at the ordinary temperature, do not lose in weight when heated to 100° C.; but upon increasing the heat, they fuse, swell, and evolve an ammoniacal salt containing phosphorus in some form, and afterwards free ammonia. There remains azophosphoric acid (easily recognized by the immediate production, in the cold, of the characteristic iron-salt, when mixed with a solution of the sulphate of that metal), together with some glacial phosphoric acid.

Oxidizing agents have little action upon this crystalline acid: nitric acid even may be boiled upon it long without causing decomposition. Strong sulphuric acid, in the cold, has likewise no effect, beyond that of dissolving it.

As the crystals themselves were not very definite in appearance, and as some which had been put aside for a few months were found to have undergone a spontaneous change, with the formation of



ammoniacal salts, it was feared that no good analytical results were likely to be obtained from the acid itself. Its insoluble salts, however, promised better. Upon the addition of nitrate of baryta to a solution of the crystals, a white, flocculent salt is formed. This was analyzed; but such differences in the estimation of the base as 43 and 60 per cent, soon showed that no reliance was to be placed upon the uniformity of composition of this precipitate.

One property of this crystalline acid is to produce azophosphoric acid, when its solution is boiled with certain metallic salts. If the sulphate of the sesquioxide of iron be added to an aqueous solution of these crystals, no precipitate appears, proving that azophosphoric acid does not pre-exist in them; but it is instantly formed on boiling.

Again, if the acid be nearly neutralized by an alkali, and boiled with a solution of most other metallic salts, such as sulphate of copper, the azophosphate of the metallic base gradually precipitates.

Now this is precisely what occurs when an azophosphate is produced, as described in my former Paper. It was there directed that chlorophosphuret of nitrogen should be dissolved in alcohol, and decomposed by ammonia; the salts thus obtained were then to be evaporated to dryness, redissolved in water, and boiled with the sulphate of iron, or other metallic salt, till the azophosphate was precipitated. It seems probable, therefore, that the alkali accomplishes instantaneously the same decomposition which the chlorophosphuret of nitrogen slowly undergoes when dissolved in ether; and that the resulting salts are really the combinations of hydrochloric acid and the new crystallizable acid with the alkali employed. And this supposition is confirmed by the fact that the neutral or slightly acid solution, obtained by decomposing chlorophosphuret of nitrogen by an alkali, does yield similar flocculent precipitates, when mixed with solutions of baryta or lime salts; and if nitrate of silver be employed, a precipitate is formed, which is very readily acted upon by the light, and mixed with a large quantity of chloride of silver.

*Baryta-salt.*—Various attempts were made to analyze the baryta-salt. Some peculiarities exhibited in its production must be noticed. If a strong solution of nitrate of baryta or chloride of barium, be added to a slightly acid solution, a precipitate falls; but a more copious precipitate is obtained from a neutral or slightly ammoniacal solution; yet the precipitate is itself wholly soluble in a considerable amount of ammonia, and may be regained (perhaps in an altered condition) by evaporating off the large excess. The salt in question

is to some extent soluble in water, but the presence or absence of different salts in the liquid, appears greatly to affect its solubility.

The results of analyses of different preparations of this baryta-salt are highly variable, and I shall merely give the percentages without details. The base was of course always weighed as sulphate, and thus there can be little doubt respecting the accuracy of its determination; but, although various means were resorted to for the estimation of the phosphorus and nitrogen, I never felt satisfied that the whole amount of either was obtained.

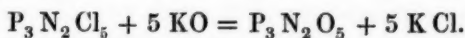
The last four determinations recorded below form a series. Some chlorophosphuret was decomposed by means of alcohol and ammonia, and evaporated to dryness; when redissolved, it was slightly acid. A concentrated solution of chloride of barium was added, which precipitated a white flocculent salt: this furnished result No. 4. Ammonia added to the filtered solution caused a small precipitate, which yielded No. 5. The solution separated from this was warmed, and more ammonia was added: a similar precipitate fell, which was collected, and the solution, on standing, yielded a fresh quantity of salt. These precipitates furnished, respectively, Nos. 6 and 7. The method adopted for analysis was first to heat the salt, previously dried at 100° C., in a tube *per se*, and collect the water and ammonia evolved in a tube filled with sticks of potash, and a Will's hydrochloric-acid apparatus annexed to it. The resulting mass was then dissolved in dilute acid, and the baryta precipitated as sulphate; the solution, containing then the free acid not already decomposed, was nearly neutralized by carbonate of potash, and was boiled with sulphate of sesquioxide of iron, to convert as much as possible into the azophosphate. This was separated, and the liquid evaporated down, and fused with hydrate of potash. The gas evolved was collected, and the phosphoric acid contained in the alkaline mass was estimated as usual. In No. 4. the salt was not heated *per se*.

	I.	II.	III.	IV.	V.	VI.	VII.
Baryta	49·8	52·2	51·4	45·0	46	53·2	55·0
Phosphorus	10·8	14·0	19·0	15·9	—	22·4	17·3
Nitrogen	1·1	—	—	6·6	—	5·0	5·4
Hydrogen	—	—	—	—	1	0·7	0·8

The salt evidently varies in composition. There appeared no reason for believing that salts of other bases would be more uniform, and the difficulty of obtaining a quantity of the chlorophosphuret of

nitrogen rendered me little disposed to undertake more analyses of so unpromising a character.

If the formation of the acid in question be considered, we can scarcely entertain a doubt as to its true composition. It is formed from chlorophosphuret of nitrogen, by the action of alkalis; the alcohol, which is necessary for the success of the process, appears to play no other part than that of a solvent. The whole of the chlorine is removed, as I have found by direct experiment; but the phosphorus and nitrogen seem to give rise to no secondary products. No phosphoric, phosphorous, or nitric acid, is formed; nor have I been able to detect ammonia, when potash has been the alkali employed; neither is there any gaseous body evolved. We can only imagine, therefore, that the chlorine of the chlorophosphuret is replaced by oxygen, thus:



Again, in the decomposition of chlorophosphuret of nitrogen by means of ether, no other bodies appear to be formed, except hydrochloric acid and the acid in question, the aromatic liquid, of which a larger or smaller quantity is usually found accompanying the preparation, being a secondary product unessential to the decomposition. This is consistent with the view just expressed, but it supposes that the decomposition depends upon the water present in the organic solvent. In order to test this important point, some crystals were dissolved in *anhydrous* ether, and the solution kept in a well-stoppered bottle; it was then found that the chlorophosphuret remained unaltered, even after the lapse of thirty days. Nor does a solution in anhydrous ether undergo any change upon boiling. The ether, then, has no specific action on chlorophosphuret of nitrogen, beyond that of a solvent; it merely facilitates its coming into contact with water, and the real decomposition would appear to be:



Indeed, the presence of ether is not absolutely essential; for if some perfectly pure crystals of the chlorophosphuret be allowed to remain in distilled water for several weeks, the liquid will be found to react distinctly acid, and to be, in reality, a solution of the two acid products of decomposition given in the formula above.

Again, this acid or its compounds boiled with certain metallic salts, yield the allied body—azophosphoric acid—having the formula  $\text{P}_2\text{N O}_5$ . Now, if this last arise from  $\text{P}_3\text{N}_2\text{O}_5$ , it will simply be by the elimination of 1 atom of phosphorus, and 1 atom of nitrogen, most probably as phosphite of ammonia by the fixation of the ele-

ments of water. That ammonia is really one of the products of the decomposition, I have repeatedly satisfied myself; but I have never succeeded in obtaining clear indications of phosphorous acid; yet, when it is remembered that heat is always employed, and that metallic salts are present, it is scarcely to be wondered at that so oxidizable a substance should be converted into phosphoric acid; and that is always found.

Yet, in order to have numerical proof that this new acid really did contain phosphorus and nitrogen in the proportions here assigned to it, the last-mentioned reaction was taken advantage of. Some crystals, formed by the spontaneous evaporation of an ethereal solution of chlorophosphuret of nitrogen, and purified by washing with alcohol, were dried, *in vacuo*, over sulphuric acid. They were then dissolved in water, and sulphate of the sesquioxide of iron was added; on boiling, azophosphate of iron separated, which was collected and dried *in vacuo*. The filtered solution was gently evaporated to dryness, and the resulting salt was fused with hydrate of potash in a silver tube, and the evolved ammonia and resulting phosphoric acid were estimated as described in previous experiments. 0.219 grm. of the crystallized acid yielded 0.217 grm. of azophosphate of iron ( $\text{Fe}_2\text{O}_3, \text{P}_2\text{NO}_5, 5\text{HO}$ ), and afterwards 0.1205 grm. of ammonio-chloride of platinum and 0.0655 grm. of phosphoric acid, which is:

	As azophosphate.	Not as azophosphate.
Phosphorus . . .	0.0571	0.0291
Nitrogen . . .	0.0125	0.0078

It appears, then, that two-thirds of the phosphorus is removed in the form of azophosphate of iron, while the remaining one-third combines with oxygen. There is certainly not as much nitrogen found in the form of ammonia as in the azophosphate; but when it is borne in mind that the whole of the ammonia is never obtained by the process followed, I conceive the experiment lends its full weight of evidence to the view given above, of the formation of azophosphoric acid.

A second portion of acid was likewise analyzed by boiling with iron-salt, and subsequent fusion with potash. 0.463 grm. of the crystals dried *in vacuo*, yielded 0.414 grm. of azophosphate of iron, 0.440 grm. of ammonio-chloride of platinum, and 0.148 grm. of phosphoric acid.

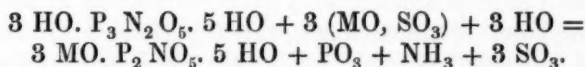
If the whole amounts found of the two elements—phosphorus and nitrogen—be reckoned to 100 parts, we have:

	I.	II.
Phosphorus . . .	39·36	38·01
Nitrogen . . .	9·27	11·08

which indicates at least 8 atoms of water. Reasons will presently be assigned for believing this acid to be tribasic. The formula  $3 \text{ HO}, \text{P}_3 \text{N}_2 \text{O}_5, 5 \text{ HO}$ , would require :

Phosphorus . . .	96	40·67
Nitrogen . . .	28	11·86
Oxygen . . .	40	16·95
Water . . .	72	30·51
	<hr/> 236	<hr/> 100·00

This view of the constitution of the acid itself, simplifies our conception of the reaction by which azophosphoric acid is produced. It will be :



As this crystalline acid is analogous to azophosphoric acid, but differs from it in the same manner as the latter differs from phosphoric acid, namely, by the addition of PN, I shall designate it—Deut-azophosphoric Acid.

*Deutazophosphate of baryta.*—This salt has been already described: it varies in composition. In the experiment which afforded the series of analyses Nos. 4 to 7, the base increased in amount, and eventually a salt was obtained, having very nearly the composition  $3 \text{ BaO}, \text{P}_3 \text{N}_2 \text{O}_5, 3 \text{ HO}$ .

	Calculated.	Found.	
		VI.	VII.
Baryta . .	230	54·63	53·2
Phosphorus .	96	22·80	22·4
Nitrogen . .	28	6·65	5·0
Hydrogen . .	3	0·71	0·7
Oxygen . .	64	15·20	—
	<hr/> 421	<hr/> 100·00	

This baryta-salt, like the azophosphate, is decomposed by heat, turning black, and evolving, at the same time, aqueous vapour, ammonia, and free oxygen, which has arisen from the decomposition of water, to supply the hydrogen which has entered into combination

with part of the nitrogen. Thus, in the two analyses just recorded, the loss in weight caused by heating the salt, coincided very nearly with that which was calculated from the amounts of ammonia and water given off:

	Water.	Nitrogen.	Decomposed water.	Theoretical loss.	Actual loss.
Exp. VI.	0.0065	+ 0.0045	+ 0.001	$\times 9 = 0.020$	0.023
Exp. VII.	0.0055	+ 0.0033	+ 0.0007	$\times 9 = 0.015$	0.015

*Deutazophosphate of Ammonia.*—In the decomposition of chlorophosphuret of nitrogen by an alcoholic solution of ammonia, we obtain this salt mixed with chloride of ammonium. Now, the amount of chloride of ammonium produced from a known weight of the chlorophosphuret can be easily calculated. If, therefore, we subtract the amount of it from the weight of the dry salts, we obtain the weight of the deutazophosphate which has been formed. During the investigation of azophosphoric acid, the decomposition of the original chlorophosphuret of nitrogen was thrice performed quantitatively. Excess of ammonia was employed, and the resulting salts were dried in a water-bath.

Exp. I. 0.2135 grm. of  $P_3 N_2 Cl_5$  yielded 0.387 grm. of ammoniacal salts.

Exp. II. 0.2553                   "                   "                   0.469   "                   "

Exp. III. 0.7035                   "                   "                   1.2505   "                   "

Now, 0.2135 grm. of  $P_3 N_2 Cl_5$  consists of 0.088  $P_3 N_2$ , and 0.1255 Cl, which would produce 0.1895  $NH_4 Cl$ ; and this number subtracted from 0.387 leaves 0.1975, as the amount of deutazophosphate of ammonia.

Therefore, Exp. I. 0.088 grm. of  $P_3 N_2$  yields 0.1975 grm. of ammonia-salt.

Similarly, Exp. II. 0.105                   "                   "                   0.2425   "                   "

and           Exp. III. 0.2894                   "                   "                   0.6264   "                   "

These numbers are in the ratio of—

Exp. I.	100	:	224.4
Exp. II.	100	:	230.9
Exp. III.	100	:	216.4

So large an increase of weight tends to show that at least three equivalents of oxide of ammonium have combined with the deutazophosphoric acid. A formula deduced from such slight grounds is of



course problematical, and the variations in the three results (mainly attributable to the very deliquescent character of the salt) are beyond the range of a single equivalent of water; yet, if we suppose the ammonia-salt to have a composition similar to that of the baryta-salt, namely,  $3 \text{NH}_4 \text{O} \cdot \text{P}_3 \text{N}_2 \text{O}_5 \cdot 3 \text{HO}$ , the increase upon the original  $\text{P}_3 \text{N}_2$  would be as—

$$100 : 216.9$$

a number coincident with the lowest and most trustworthy result afforded by experiment.

If ammonia be added to a strong solution of the pure acid, a mass of crystals immediately separates; upon the application of heat this crystalline precipitate redissolves, and there remains a neutral salt, which may be evaporated to a syrup without crystallizing. If this neutral substance be dissolved in a small quantity of water, the addition of strong ammonia will again cause the precipitation of a crystalline salt. Deutazophosphate of ammonia is very deliquescent in damp air; when heated *per se*, it swells up greatly, and evolves ammoniacal gas, whilst azophosphoric acid is found among the products in the fixed residue.

*Deutazophosphate of Silver.*—A portion of the flocculent, difficultly soluble silver-salt, mentioned at the commencement of this paper, was found to contain only 53.2 per cent of oxide of silver,—which is much less than a composition similar to that of the baryta-salt would require.

Deutazophosphoric acid is capable of forming white flocculent salts with the earths,—baryta, strontia, lime, and magnesia, and with oxide of lead; but I have not succeeded in preparing salts of this acid containing such metals as iron, copper, or zinc, either by double decomposition, or by presenting the freshly precipitated oxide to a solution of the acid itself.

#### AMMONIO-AZOPHOSPHATE OF IRON.

An examination of this substance was undertaken principally in the hope that it would throw some light upon the function of those atoms of water, which form a constituent of the azophosphates and deutazophosphates, and which cannot be driven off, at least from the former, without destroying the salt itself.

It was stated in my previous paper, that azophosphate of iron is wholly soluble in ammonia, but that the compound thus formed is decomposed on evaporation in a water-bath. If, however, the drying be conducted at the ordinary temperature *in vacuo* over sul-

phuric acid, a deep-red mass is obtained, covering the bottom of the vessel like a varnish, and splitting up as it becomes perfectly desiccated. This substance dissolves completely in cold water, giving a red solution, neutral to test-paper.

0.2253 grm. of this substance dried *in vacuo*, decomposed by dilute hydrochloric acid, yielded 0.1645 grm. of azophosphate of iron ( $\text{Fe}_2 \text{O}_3 \cdot \text{P}_2 \text{NO}_5 \cdot 5\text{HO}$ ), and 0.120 grm. of chloride of ammonium.

Now, 0.120 grm. of chloride of ammonium is equivalent to 0.0583 grm. of oxide of ammonium, and such an amount it is which must be added to the 0.1645 grm. of azophosphate, in order to approximate the original weight of the salt, 0.2253 grm.

$$0.1645 + 0.0583 = 0.2228.$$

Or, if these numbers be reckoned to 100 parts, we have :

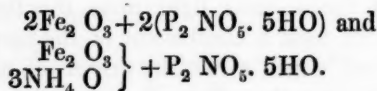
Azophosphate of iron, $\text{Fe}_2 \text{O}_3 \cdot \text{P}_2 \text{NO}_5 \cdot 5\text{HO}$ . . .	73.0
Oxide of ammonium, $\text{NH}_4 \text{O}$ . . . . .	25.8
	<hr/>
	98.8

This agrees most nearly with the numbers deduced from the formula,  $\text{Fe}_2 \text{O}_3 \cdot 3\text{NH}_4 \text{O} \cdot \text{P}_2 \text{NO}_5 \cdot 5\text{HO}$ . namely :

Azophosphate of iron . . .	243	75.70
Oxide of ammonium . . .	78	24.30
	<hr/>	<hr/>
	321	100.00

This experiment appears to indicate that the 5 atoms of combined water are not either wholly or partially basic, but are, nevertheless, intimately connected with the compound itself: yet, as 1 atom can be driven off from the iron-salt by heat, and as the azophosphate of baryta contains but 2 atoms of water, the hydrogen cannot be considered as an integral part of the formula of the acid.

Applying the phosphoric-acid theory of Messrs. Fleitmann and Henneberg to the expression of the azophosphate of iron, we shall have the formulæ :



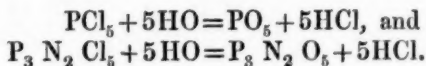
#### AROMATIC LIQUID.

It has already been stated that chlorophosphuret of nitrogen is decomposed under the influence of alcohol, giving rise to hydro-

chloric acid, and a liquid body having an aromatic odour and not miscible with water. This last substance is readily soluble in alcohol and in the essential oils. It has usually a slight yellow tinge, but I have obtained it nearly colourless. It appears incapable of being distilled without change. A portion subjected to a temperature gradually increasing, was decomposed at a little above  $100^{\circ}$  C.; a light, colourless, and highly volatile liquid came over; and afterwards a heavy oleaginous body of a very pungent odour, which was not miscible with the former. The aromatic liquid in question is not attacked by aqueous solutions of potash, nitric acid, or sulphuric acid; but it is instantly decomposed by an alcoholic solution of potash, with the formation of salts which are perfectly soluble in water, and which, when fused with an excess of the alkali, yield ammoniacal gas, whilst phosphoric acid remains in the fixed residue. The solution of the salts obtained by this decomposition of the liquid by means of any alkali, when properly neutralized, affords a baryta-salt resembling the deutazophosphate of baryta just described; if mixed with a solution of sulphate of sesquioxide of iron, it gives no precipitate at first; but on boiling, it yields the characteristic white flocculi of azophosphate of iron. The aromatic liquid then contains deutazophosphoric acid.

A portion of the liquid under examination was purified from adhering acid and water, first by carbonate of soda, and afterwards by standing over dry chloride of calcium. It was then introduced into a small glass bulb, and burnt with chromate of lead, as in the usual combustion-process for organic compounds. In consequence of the liquid becoming carbonized in the bulb, the combustion was worthless as a quantitative experiment; but it proved that the substance contained a large percentage of carbon and hydrogen; and, if the mode of its formation be considered, I think there can be little doubt that the aromatic liquid in question is *deutazophosphoric ether*.

From the reactions which have formed the subject of this paper, it appears that the so-called "chlorophosphuret of nitrogen" is a body analogous in constitution to pentachloride of phosphorus. It exhibits little or no tendency to combine with any other substance without itself undergoing decomposition; but it is resolved, by assumption of the elements of water, into hydrochloric acid and another acid—a compound of the electro-positive portion with five equivalents of oxygen.



The reaction by which it is formed when ammonia and pentachloride of phosphorus are brought together, cannot be distinctly traced. It is evidently a by-product—a result, in all probability, of the action of the newly-formed compounds of phosphorus and nitrogen upon the pentachloride. It is not found amongst the products of decomposition when pentabromide of phosphorus is heated with chloride of ammonium.

It was to be expected that a substance might exist, presenting a composition intermediate between that of pentachloride of phosphorus,  $\text{PCl}_5$ , and chlorophosphuret of nitrogen,  $\text{P}_3\text{N}_2\text{Cl}_5$ —in fact,  $\text{P}_2\text{NCl}_5$ —and which should give azophosphoric acid,  $\text{P}_2\text{NO}_5$ , when decomposed by water; but no such compound has yet been observed. Liebig and Wöhler mention a substance given off in the preparation of chlorophosphuret of nitrogen, which has a peculiar and distinct odour: I have remarked the same, but only, I believe, when the chloride of phosphorus has not been thoroughly saturated with chlorine.

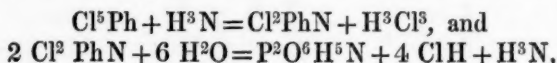
The two acids with which this investigation has made us acquainted, may be considered as the second and third terms of a series commencing with ordinary phosphoric acid, and bearing a marked resemblance to it, both in their tribasic character and in their general properties. They differ in composition from phosphoric acid, in containing its elements  $\text{PO}_5$  conjugated with  $\text{PN}$  or  $2\text{PN}$ ; and thus present another instance of that law, of which we have so many examples in organic chemistry, that the addition of any number of atoms of a certain increment will only modify the particular properties of a body, not affect its general character.

Phosphoric acid	.	.	.	$\text{PO}_5$
Azophosphoric acid	.	.	$\text{P}_2\text{N O}_5$ or $(\text{PN})$	$\text{PO}_5$
Deutazophosphoric acid	.	.	$\text{P}_3\text{N}_2\text{ O}_5$ or $(2\text{PN})$	$\text{PO}_5$

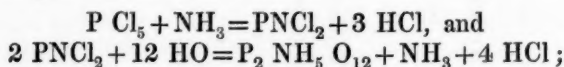
The general resemblance between these three acids, and at the same time, the gradual departure from the primitive type which the more compound acids present, may be well exhibited in a tabular form:

PHOSPHORIC ACID.	AZOPHOSPHORIC ACID.	DEUTAZOPHOSPHORIC ACID.
Hydrated acid is stable.	Hydrated acid is stable.	Hydrated acid is stable.
" " deliquescent.	" " deliquescent.	" " deliquescent.
" " glacial.	" " amorphous.	" " crystalline.
Tribasic.	Tribasic.	Tribasic.
Forms soluble salts with alkalis.	Forms soluble salts with alkalis.	Forms soluble salts with alkalis.
" insoluble salts with earths.	" insoluble salts with earths.	" slightly sol. salts with earths.
" flocculent and white salts with earths.	" flocculent and white salts with earths.	" flocculent and white salts with earths.
" insoluble salts with metals.	" insoluble salts with metals.	
" flocculent and mostly white salts with metals.	" flocculent and mostly white salts with metals.	
$\text{Fe}_2\text{O}_3$ salt insoluble in weak acids.	$\text{Fe}_2\text{O}_3$ salt insoluble in dilute acids.	
" " white.	" " white.	

*Note.*—Since writing the above, my attention has been drawn to a paragraph at the conclusion of a paper on Organic Combinations by M. Laurent, in the "Comptes Rendus" of the French Academy for September 9th, 1850. He there remarks, that the formulæ assigned by me to "Chlorophosphuret of Nitrogen" and "Azophosphoric acid" are quite inadmissible. He gives, moreover, the following as the reactions which ought to take place in their formation :



or, according to our notation,



and thus he considers my "azophosphoric acid" as "pyrophosphamic acid." In the October number of the "Comptes Rendus" of Messrs. Laurent and Gerhardt, these views, somewhat enlarged, are put forth in full detail. Yet, as these eminent chemists admit in their editorial remarks, that fresh experiments are necessary to verify their corrections, I have little doubt that the statements contained in the present paper will satisfy them that the reactions expressed by their formulæ do not really take place.

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Dec. 2, 1850.

ROBERT PORRETT, Esq., Treasurer, in the Chair.

The following presents were announced :

"Memoir on the Explosiveness of Nitre," by Robert Hare, M.D.: presented by the Author.

"Pharmaceutical Journal for December:" presented by the Editor.

"Quarterly Journal of the Geological Society for September," (No. 24, Vol. 6.): presented by the Society.

"Öfversigt af Kongl. Vetenskaps-Akademiens Förhandlingar:" Sjette Årgången, 1849.

"Kongl. Vetenskaps-Akademiens Handlingar, för år, 1848:" presented by the Royal Stockholm Academy.

"An Introduction to the Atomic Theory," by Charles Daubeny, M.D., F.R.S.: presented by the Author.



The following Papers were read :

XXX—*Analysis of Sugar Feculencies.*

By T. J. HERAPATH, F.C.S.

Ashes 13·574	Water	48·940
	Organic matter	37·486
	Carbonate of potash	0·146
	Sulphate of soda	0·155
	Chloride of sodium and chloride of potassium.	0·237
	Carbonate of lime with some carbonate of magnesia	3·964
	Sulphate of lime	1·231
	Phosphate of lime with some phosphate of magnesia	2·679
	Phosphate of iron and alumina	1·320
	Siliceous residue, &c., insoluble in acids	3·842
		<hr/> 100·000

100 grains of the dried matters were found to contain 5·42 grs. of nitrogen ; consequently, the feculencies in their normal state contain 2·805 per cent.

The exhausted animal-charcoal, from the same refinery, was found when dried, to contain 2·82 per cent of nitrogen.

XXXI.—*On a Cement for stopping the cavities of Teeth.*

By T. J. HERAPATH, F.C.S.

A good cement for stopping the cavities of carious teeth has long been a great desideratum to dentists, because, unfortunately, almost all those now known possess some disadvantage or other. Even the copper-amalgam, hitherto the one most preferred by the members of this profession, and of which the analysis and mode of preparation have been recently described by M. Pettenkofer,\* is apt to communicate a very unpleasant metallic taste to the food, and soon becomes discoloured, in consequence of the formation of a thin film of black sulphuret of copper. But in the course of the last few months, another succedaneum, the invention of an American gentleman, has been brought into notice ; and this would appear to

\* Ann. Ch. Pharm. June, 1849.

possess every requisite that could be desired. The substance referred to is an alloy of tin and cadmium. When combined with a small quantity of mercury, it becomes soft and semi-fluid, and may then be easily pressed into the cavity of the decayed tooth, where it soon solidifies into a hard, tenacious, crystalline amalgam, thus preventing the access of air to the interior of the tooth and rendering the organ fit for the purposes of mastication. Being at the same time of a dull white colour, similar in appearance to frosted silver, and not liable to become tarnished, close scrutiny is required in order to detect its presence. The great advantage of this latter property need not be pointed out.

When about to be employed, the alloy in fine powder is mixed up by the operator in the palm of his hand, with from two and a half to three times its weight of mercury, or such a quantity as will suffice to render it perfectly soft, when it is immediately pressed into the cavity in the enamel, the latter having been previously cleansed and dried by the ordinary method.

The alloy above-described, as may be naturally supposed, is readily acted upon by acids, even by the diluted vegetable acids, which gradually dissolve out the cadmium. But as the salts of cadmium do not appear to produce any injurious action upon the system, unless taken in large quantity, of course no ill effects need be expected to result from this circumstance.

This metallic combination of tin and cadmium presents us with another interesting example of the effects of crystallization and amorphism on the physical properties of bodies. As in the case of the copper-amalgam before adverted to, the specific gravity does not appear to vary in the transition from the amorphous to the crystallized condition, as the amalgam, when hard, occupies very nearly, if not exactly, the same space that it does when soft and fluid.

In conclusion I may observe, it has been found that, the proportion of the cadmium may be considerably reduced without altering the physical properties of the compound. A mixture of 5 parts of cadmium and 7 to 8 of tin is the best, and has been found to answer remarkably well.

A quantity of the cement in question was placed in my hands some time since by a friend who wished to learn the nature of its components. Upon subjecting it to analysis, it was found to consist of tin and cadmium in the following proportions:

8.90	grs.	gave	3.962	grs. of $\text{SnO}^2$	and	6.629	grs. of $\text{CdO}$ .
10.00	"	"	4.460	" of $\text{SnO}^2$	"	7.429	" of $\text{CdO}$ .
10.00	"	"	4.630	" of $\text{SnO}^2$	"	7.422	" of $\text{CdO}$ .

It would therefore appear to be composed of:

	I.	II.	III.	Mean.
Tin . . .	34·899	34·960	34·980	34·946
Cadmium .	65·061	65·010	64·950	65·007

and must therefore be considered as an alloy of these two metals in the proportion of one atom of the former to two of the latter.

The best mode of preparing it, I find to be as follows:—Melt a quantity of bees'-wax in a pipkin over the fire, and then throw in the cadmium; by these means, the loss of cadmium which would otherwise result from oxidation is avoided. So soon as the metal is completely fused, add the tin in small pieces till a perfectly homogeneous alloy is formed. This can be afterwards granulated in the usual manner, or by introducing it into a wooden or iron box, and shaking it up rapidly while it still remains in the fluid state.

Since the above was written, I have analysed another and somewhat similar cement, which was stated by the inventor to be composed of platinum and tin. A quantitative examination, however, proved it to possess the following composition in 100 parts:

Silver . . . . .	73·188
Tin . . . . .	21·127
Zinc . . . . .	slight traces
Platinum with very slight traces of gold .	5·685
	<hr/>
	100·000

### XXXII.—On the Chemical Constitution and Nature of Organic Radicals.

BY H. KOLBE., PH. D., F.C.S.

Do compound radicals exist in organic combinations, exercising therein the functions of simple elements, and combining, like the latter, with oxygen, sulphur, chlorine, &c., in certain atomic proportions, to form oxides (acids), sulphides and chlorides?

Do these compound radicals consist of *unalterable* groups of atoms, or can the substitution of their hydrogen by chlorine, bromine, hyponitric acid, &c., be effected, unaccompanied by the disturbance of chemical equilibrium?

Is it at variance with the principles of the electro-chemical theory, that elements of such different chemical properties, as hydrogen and chlorine, should displace each other; and that oxygen, chlorine, and similar bodies of decidedly electro-negative character, should rank among the constituents of organic radicals?

The above questions, first set on foot by the discovery of chloracetic acid, have been answered in various ways, and most decidedly and minutely by Berzelius, in the correspondence that lasted for some years between himself and Dumas. These interesting discussions were unfortunately interrupted by the death of the first-named chemist, without any understanding or approximation of views being effected, so that the opinions of chemists are, to this day, widely at variance with regard to the above points. Berzelius, and with him the greater number of German chemists, have, as is well known, adhered to their opinion of the existence of compound radicals, the correctness of which they have considered as proved by the successful isolation and the chemical properties of cyanogen and cacodyl. In addition to this, Berzelius obstinately defended the principle against all attacks made by adherents to the theory of substitution, that organic radicals were unalterable groups of atoms; that substitution could not be effected in them without a thorough alteration of their chemical constitution, least of all the substitution of hydrogen by bodies of such prominently electro-negative properties as chlorine, bromine, oxygen, &c.; and that the assumption of organic radicals containing oxygen or chlorine, was in contradiction to the principles of the electro-chemical theory.

On the other hand, Dumas, without distinctly stating whether, indeed, he assumes the existence of organic radicals, has maintained the principle that compounds, containing an equal number of equivalents arranged in a like manner, are possessed of the same fundamental properties, and that the function exercised by an element in organic combination is not dependent upon its original properties, but rather upon the position which it occupies in the compound. Both chemists agree in the opinion, that the assumption of a replacement of the positive hydrogen by the negative chlorine in a compound radical, is at variance with the electro-chemical theory, because, according to this theory, the nature of a compound cannot be considered as independent of the chemical nature of its constituents. This accordance of opinion, with respect to the latter point, has been most probably the principal reason why the question as to the immutability of organic radicals has not been made the subject of investigation to the degree that it merits.

It may be considered as beyond all doubt that the theory of radicals in its present state no longer suffices to furnish proper explanations of the innumerable metamorphoses resulting from so-called substitution, and that, by a continued adherence to the unchangeability of compound radicals, the secure foundation resulting from the theory of radicals becomes continually weakened. We are, indeed, at the present moment, almost forced by facts to assume that organic radicals are alterable groups of atoms, in which chlorine, bromine, hyponitric acid, &c., may enter in the place of hydrogen, the molecular grouping of their atoms remaining unchanged, and secondary radicals being thus produced, which are possessed, in part, of properties similar to those of the primary ones. Instead of at once discussing the question, whether and how far this mode of viewing may be made to accord with the electro-chemical theory, I will endeavour, in the following pages, to apply this hypothesis to a series of organic combinations, and more particularly to those, the comportment and metamorphoses of which it has been most difficult to explain by the theory of radicals as it now stands.

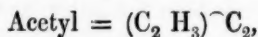
The difficulty of bringing the behaviour of acetic acid with chlorine, and its reproduction from chloracetic acid, to accord with the assumption of an unalterable acetyl-radical of the formula  $C_4 H_3$ , first led Berzelius to construct the hypothesis, that acetic acid and chloracetic acid might be conjugated oxalic acids, the one containing methyl, and the other sesquichloride of carbon as adjuncts, and that the conversion of acetic into chloracetic acid was solely due to a metamorphosis of the adjunct, while the oxalic acid itself remained unaltered.

Whatever may be the opinion entertained as to the value of this hypothesis, it cannot be denied that the pre-existence of methyl in acetic acid has received a high degree of probability from facts, most of which were only subsequently discovered. Independent of the analogy existing between acetic and chloracetic acid on the one hand, and between methylo-hyposulphuric acid and sesqui-chlorocarbohyposulphuric acid on the other, to which I have already referred in a previous paper,\* the conversion of acetate of ammonia into cyanide of methyl, and the reproduction of acetic acid from the latter, as also the decomposition of acetic acid, by the galvanic current, into methyl and carbonic acid, can scarcely be satisfactorily interpreted, otherwise than by the assumption of the existence of methyl as a component part of acetic acid.

\* Ann. Ch. Pharm. d. LIV, 148, ff; Chem. Soc. Mem. II, 360.

It has not as yet been attempted to extend the above hypothesis to the remaining combinations of acetyl, which, if acetic acid were methyloxalic acid, must evidently have a composition corresponding to this view. The result of such an attempt would be the necessity of assuming the existence in aldehyde, acetyloous acid, chloride of acetyl, &c., of the partly hypothetical bodies  $C_2O$ ,  $C_2O_2$  and  $C_2Cl_3$  coupled with methyl. We should likewise be forced to assume that, in the terchloride of acetyl (the so-called dichlorinated chloride of ethyl), which, according to Regnault, may be converted, by continuous boiling with alcoholic potassa, into acetic acid and chloride of potassium, the sesquichloride of carbon, considered as combined therein with methyl, must differ considerably in its properties from the same substance when uncombined, as the latter cannot be converted, by similar treatment, into the corresponding oxygen-compound, oxalic acid; moreover a further extension of the hypothesis to the remaining compounds allied to acetic acid—for example, to the other members of the series  $(C_2H_2)_nO_4$ , as also to benzoic acid and its homologues, &c., would show that, instead of viewing them as oxides of compound radicals, as hitherto, we must consider them all as conjugate oxalic acids, and finally that, of all the radicals which are partly really isolated, there would be few or none remaining. Even cacodylic acid, if the replacement of a portion of its hydrogen by chlorine be accomplished, as there is little doubt it will, must no longer be considered as an oxygen-compound of cacodyl, but perhaps as arsenious acid conjugated with two equivalents of methyl.

If, however, we adhere less strictly to the immutability of organic radicals, another hypothesis, very nearly allied to the former, of the chemical constitution of acetic acid, and the acetyl-compounds in general, presents itself, possessing the advantages of the former, without sharing its defects, namely: *that an acetyl-radical really exists in the acetyl-compounds; that it must not, however, be considered as a group of four equivalents of carbon and three equivalents of hydrogen, the four carbon equivalents of which possess equal functions, but that it should rather be viewed as a compound of two equivalents of carbon, and methyl as the adjunct:*



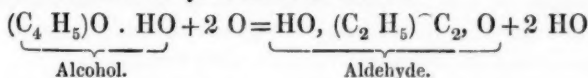
*in which the  $C_2$  presents the exclusive point of action for the powers of affinity of oxygen, chlorine, &c.*

According to this view, the composition of the acetyl-compounds, with which we are as yet acquainted, would be expressed by the following rational formulæ:

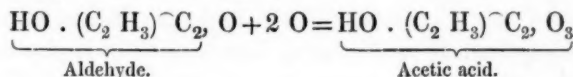


Subacetyloous acid . . .	HO . (C <sub>2</sub> H <sub>3</sub> ) <sup>^</sup> C <sub>2</sub> ,	O	(aldehyde).
Acetyloous acid . . .	HO . (C <sub>2</sub> H <sub>3</sub> ) <sup>^</sup> C <sub>2</sub> ,	O <sub>2</sub>	
Acetylic acid . . .	HO . (C <sub>2</sub> H <sub>3</sub> ) <sup>^</sup> C <sub>2</sub> ,	O <sub>3</sub>	(acetic acid).
Terchloride of acetyl . . .	(C <sub>2</sub> H <sub>3</sub> ) <sup>^</sup> C <sub>2</sub> ,	{ Cl <sub>3</sub>	( <i>éther hydro-chlorique-bichloruré</i> ).
Dinoxamide of acetyl . . .	(C <sub>2</sub> H <sub>3</sub> ) <sup>^</sup> C <sub>2</sub> ,	{ O <sub>2</sub> NH <sub>2</sub>	(acetamide).
Oxydichloride of acetyl . . .	(C <sub>2</sub> H <sub>3</sub> ) <sup>^</sup> C <sub>2</sub> ,	{ O Cl <sub>2</sub>	( <i>éther bichloruré</i> ).
Oxydisulphide of acetyl . . .	(C <sub>2</sub> H <sub>3</sub> ) <sup>^</sup> C <sub>2</sub> ,	{ O S <sub>2</sub>	( <i>éther sulfuré</i> ).
Oxysulphochloride of acetyl	(C <sub>2</sub> H <sub>3</sub> ) <sup>^</sup> C <sub>2</sub> ,	{ O S Cl	( <i>éther chloro-sulfuré</i> ).

The assumption of this conjugate acetyl-radical in aldehyde and acetic acid, renders it evidently necessary that the interpretation hitherto given to the process of acetification should be slightly modified. The action of the oxygen on the alcohol effects probably, at first, the splitting of ethyl into methyl and the carbo-hydrogen C<sub>2</sub> H<sub>2</sub>, the elimination of which from organic compounds belongs to the most common phenomena. At the moment of its liberation it undergoes a further decomposition; as the hydrogen becomes oxidised, the two equivalents of carbon immediately reunite with the methyl, forming the conjugate acetyl-radical (C<sub>2</sub> H<sub>3</sub>)<sup>^</sup>C<sub>2</sub>, with which the oxygen of the oxide of ethyl remains combined:

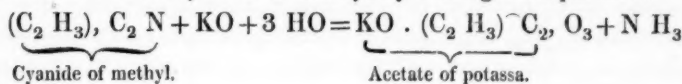


The conversion of aldehyde into acetic acid by the direct assimilation of two equivalents of oxygen,

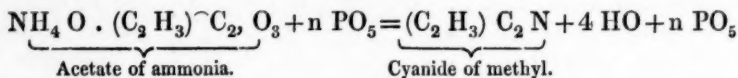


must be considered, as of old, as a pure process of oxidation.

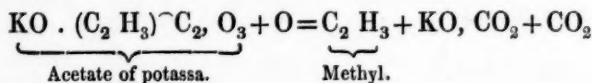
It appears to me that all other relations of acetic acid to different compounds may be explained in an equally satisfactory manner by assuming it to be composed according to the above rational formula. Its formation from cyanide of methyl by boiling with potassa:



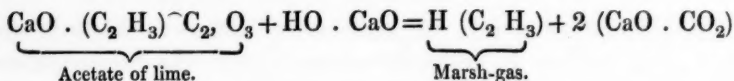
the decomposition of acetate of ammonia, by distillation with phosphoric acid, into cyanide of methyl and water :



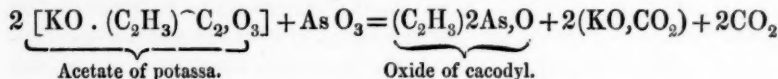
the decomposition of an aqueous solution of acetate of potassa, at the oxygen-pole of the galvanic current, into methyl and carbonic acid :



the conversion of acetic acid, by heating its lime-salt with hydrate of lime into carbonic acid and marsh-gas (hydride of methyl) :



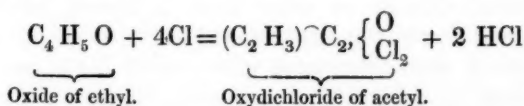
and finally, the formation of oxide of cacodyl, by the distillation of acetate of potassa with arsenious acid :



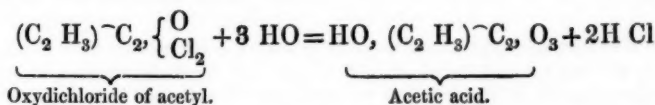
All these decompositions are most simply and naturally expressed by the above equations. I consider it at present impossible to explain the formation of acetone from acetic acid, as we are as yet quite in the dark with regard to its rational composition, and, indeed, have not even established its empirical formula with certainty.

The opinion, defended with so much warmth by the adherents to the theory of substitution, that the so-called dichlorinated oxide of ethyl still possessed the constitution of oxide of ethyl, does now scarcely need any refutation. Not only do the close relations borne by this compound to acetic acid, into which it is converted by lengthened contact with water, almost preclude a doubt of its belonging to the acetyl-series, but it is of itself more than probable that the oxide of ethyl would undergo a similar metamorphosis by the action of chlorine as with oxygen. The action of chlorine on oxide of ethyl likewise appears to consist, in the first instance, of a splitting of the ethyl-group into methyl and  $\text{C}_2 \text{H}_2$ , which is followed by the immediate decomposition of the latter carbo-hydrogen, and the formation of  $(\text{C}_2 \text{H}_3)^{\wedge} \text{C}_2$ , together with hydrochloric acid ; this radical, remaining in combination with the oxygen of the oxide of ethyl, assi-

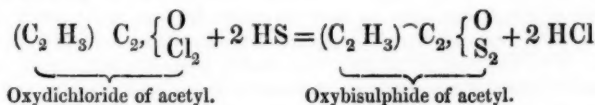
milates, in addition, two equivalents of free chlorine, and thus becomes  $(C_2 H_3)^{\sim}C_2, \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$ , *i. e.*, oxydichloride of acetyl, according to the following equation :



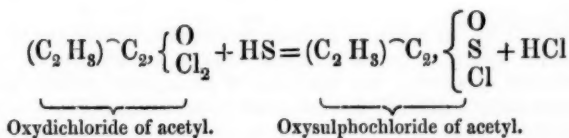
The same mode of viewing may be applied with facility to the decomposition of this acetyl-compound by water or alkalis, into acetic and hydrochloric acids :



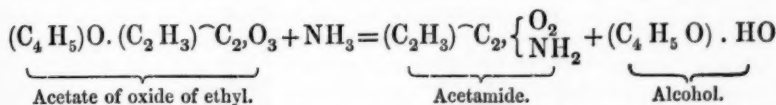
and its conversion into oxybisulphide of acetyl (éther bisulfuré), and oxysulphochloride of acetyl (éther chlorosulfuré), by the action of hydrosulphuric acid :



and



To these acetyl-combinations must still be added the dinoxamide of acetyl  $(C_2 H_3)^{\sim}C_2, \left\{ \begin{smallmatrix} O_2 \\ NH_2 \end{smallmatrix} \right.$ , the formation of which, from acetate of oxide of ethyl and ammonia, is explained by the following equation :



It can scarcely admit of a doubt that the product of decomposition of chloride of ethyl, corresponding to the dichlorinated oxide of ethyl, namely, the so-called dichlorinated chloride of ethyl, possesses a constitution similar to that of the former, and is therefore the true

terchloride of acetyl,\*  $(C_2 H_3)^{\cdot}C_2, Cl_3$ , although it exchanges its chlorine for oxygen with much greater difficulty, and requires long continued boiling with alcoholic potassa for its complete conversion into acetic acid.

By the action of chlorine on ether there is formed, according to Malaguti, in addition to the dichlorinated oxide of ethyl, a second body, the so-called semi-chlorinated ether, which Malaguti did not succeed in separating and purifying, respecting the existence of which, however, his experiments leave no doubt. This substance corresponds with the chloride of aldehyde, discovered by Regnault, in so far, that both may, from their empirical composition, be considered as ethyl-compounds, the former as the oxide of ethyl, the latter as the chloride,

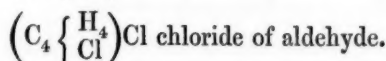
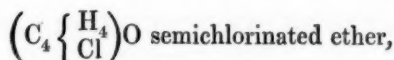
\* The substance originally named *chloride of acetyl*, is the gaseous body  $(C_4 H_3 Cl)$ , formed by the treatment of the oil of olefiant gas with alcoholic solution of potassa. The product obtained by the action of pentachloride of antimony on this gas, isomeric with the dichlorinated chloride of ethyl, has been named by Berzelius, *superchloride of acetyl*; to the dichlorinated chloride of ethyl itself, he has given the name, *superchloride of paracetyl*. It might appear from this, that the superchloride of acetyl of Berzelius, obtained from the oil of olefiant gas, was the true terchloride of acetyl, corresponding to acetic acid, while the so-called superchloride of paracetyl, obtained from chloride of ethyl, was only an isomeric compound, not really belonging to the acetyl-series. If it be considered, however, that the latter substance permits the replacement of its chlorine by oxygen, thus passing over into acetic acid, while the former cannot be directly converted into acetic acid, or any other member of the acetyl-series, there can be no doubt, whatever, that the dichlorinated oxide of ethyl (superchloride of paracetyl) is the true acetyl-compound, namely, the terchloride of acetyl  $(C_2 H_3)^{\cdot}C_2, Cl_3$ .

The gas obtained by the action of alcoholic potassa upon olefiant gas, the so-called, chloride of acetyl appears to me to belong as little to the acetyl-series, as the so-called superchloride of acetyl. The isomerism of its supposed radical with acetyl, may however be easily explained, if we consider it, as hitherto, to be a body  $(C_4 H_3)$  homologous to allyl  $(C_3 H_3)$ , for which I propose the name of *vinyl*, as suggestive of its origin (comp. *Handwörterbuch der Chemie*, Bd. v. p. 548, ff). The olefiant gas may be considered as the hydrogen-compound of this radical, or as hydride of vinyl, consisting of  $\frac{1}{2}$  volume of vinyl-vapour and  $\frac{1}{2}$  volume of hydrogen, which corresponds perfectly with the observed specific gravity, assuming a condensation of 2 vols. carbon-vapour and 3 vols. hydrogen to 1 volume, in vinyl:

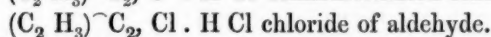
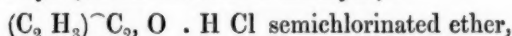
2 vols. carbon-vapour . . .	1.658.
3 „ hydrogen . . . . .	0.207.
<hr/>	
1 vol. vinyl gas . . . . .	1.865.
$\frac{1}{2}$ „ vinyl gas . . . . .	0.933.
$\frac{1}{2}$ „ hydrogen . . . . .	0.034.
<hr/>	
1 vol. hydride of vinyl . . .	0.967.

Assuming with Liebig, the oil of olefiant gas to be a combination of hydrochloric acid with the chloride of the radical vinyl, and admitting the possibility of a substitution of

in each of which one equivalent of hydrogen is replaced by one of chlorine :



As long, however, as this view is unsupported by facts, I consider it much more probable that these compounds possess a composition corresponding to the hydrochlorates of oxide of vinyl and of chloride of vinyl (comp. note, p. 376), being therefore combinations of hydrochloric acid with oxide of acetyl (in the semichlorinated ether), and chloride of acetyl (in the chloride of aldehyde) :



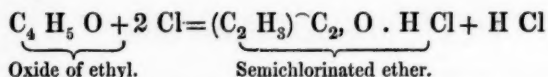
the hydrogen in vinyl itself by chlorine, the composition of the substances derived from olefiant gas, may be best expressed by the following rational formulæ :

	Vinyl = $C_4 \begin{smallmatrix} H_3 \\ H \end{smallmatrix}$	
Hydride of vinyl . . .	$(C_4 \begin{smallmatrix} H_3 \\ H \end{smallmatrix}) H$	olefiant gas.
Hydrochlorate of chloride of vinyl . . .	$(C_4 \begin{smallmatrix} H_3 \\ Cl \end{smallmatrix}) Cl, H Cl$	chloride of elayl (Berzelius).
Chloride of vinyl . . .	$(C_4 \begin{smallmatrix} H_3 \\ Cl \end{smallmatrix}) Cl$	chloride of acetyl (Berzelius).
Hydrochlorate of chloride of chlorovinyl . . .	$(C_4 \left\{ \begin{smallmatrix} H_2 \\ Cl \end{smallmatrix} \right\} Cl, H Cl$	superchloride of acetyl (Berzelius).
Chloride of chlorovinyl . . .	$(C_4 \left\{ \begin{smallmatrix} H_2 \\ Cl \end{smallmatrix} \right\} Cl$	chloride of formyl (Berzelius).
Hydrochlorate of chloride of dichlorovinyl . . .	$(C_4 \left\{ \begin{smallmatrix} H \\ Cl_2 \end{smallmatrix} \right\} Cl, H Cl$	superchloride of formyl (Berzelius).
Hydrochlorate of chloride of trichlorovinyl . . .	$(C_4 \begin{smallmatrix} Cl_3 \\ Cl \end{smallmatrix}) Cl, H Cl$	
Hydrochlorate of oxide of vinyl . . .	$(C_4 \begin{smallmatrix} H_3 \\ O \end{smallmatrix}) O, H Cl$	oxychloride of elayl (Berzelius).
Hydrobromate of bromide of vinyl . . .	$(C_4 \begin{smallmatrix} H_3 \\ Br \end{smallmatrix}) Br, H Br$	bromide of elayl (Berzelius).
Hydriodate of iodide of vinyl . . .	$(C_4 \begin{smallmatrix} H_3 \\ I \end{smallmatrix}) I, H I$	iodide of elayl (Berzelius).
Iodide of vinyl . . .	$(C_4 \begin{smallmatrix} H_3 \\ I \end{smallmatrix}) I$	iodide of acetyl (Berzelius).

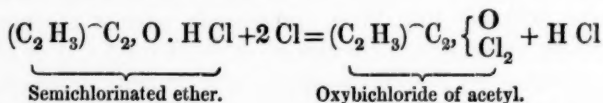
The conversion of the substance mentioned under the name of hydrochlorate of chloride of trichlorovinyl, and discovered by Pierre (Ann. Ch. Phys. [3] XXI. 429), into the so-called protochloride of carbon ( $C_2 Cl_2$ , or  $C_4 Cl_4$ ), by boiling with alcoholic potassa, is probably accompanied by an alteration in the arrangement of the elements, ( $C_4 Cl_3$ ) Cl to  $(C_2 Cl_3)^{\wedge} C_2, Cl$  (chloride of trichloroacetyl), the latter formula expressing the rational composition of protochloride of carbon, as I shall presently endeavour to show.

The sulphur-compounds of vinyl require a more careful examination than they have hitherto been subjected to. The sulphides of elayl described by Löwig and Weidmann were doubtless impure substances, containing an admixture of sulphur. It might be interesting to examine the behaviour of chloride of vinyl with sulphocyanide of potassium, as a sulphocyanide of vinyl ( $C_4 H_3$ ) Cy  $S_2$ , corresponding to oil of mustard ( $C_6 H_5$ ) Cy  $S_2$ , might possibly be produced under these circumstances.

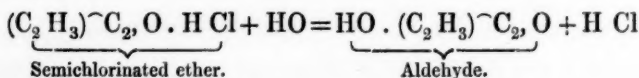
By this assumption, the formation of semi-chlorinated ether from oxide of ethyl:



its conversion into oxybichloride of acetyl (bichlorinated oxide of ethyl) by treatment with chlorine:



and its decomposition by water into aldehyde and hydrochloric acid.

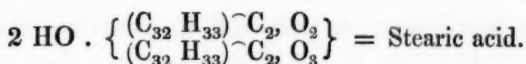


may be explained in a simple and perfectly satisfactory manner.

It may be regarded as self-evident that a hypothesis constructed upon the constitution of acetic acid, or any other member of the series of fatty acids, must likewise admit of application to the remaining members of that series. If, therefore, we consider acetic acid as the oxide of the conjugate radical  $(\text{C}_2 \text{H}_3)^{\sim} \text{C}_2$ , it follows naturally that we must assume the existence of conjugate radicals analogous to acetyl, in propionic, valeric, margaric, formic acids, &c. Indeed, in an attentive examination of these compounds, I have not met with any fact that was in contradiction with the above hypothesis; and I believe that I do not err in expressing the conviction that the compartment of the fatty acids, from formic acid up to melissic acid, and their manifold relations to other compounds, may be better interpreted by the above hypothesis than by any one of the former views. The decomposition of valeric acid by the galvanic current into butyl ( $\text{C}_8 \text{H}_9$ ) and carbonic acid, and its formation from cyanide of butyl ( $\text{C}_8 \text{H}_9$ )  $\text{C}_2 \text{N}$  (valeronitril), are particularly well adapted to support this opinion.

The relation of stearic to margaric acid, and its bibasic nature, may be easily explained, without our being obliged to adopt the assertion made by Laurent and Gerhardt, that both these acids possess the same composition and saturating capacity, and are only two isomeric modifications, if we view stearic acid as a double acid, composed of two different oxides of margaryl  $(\text{C}_{32} \text{H}_{33})^{\sim} \text{C}_2$ , namely:  $\text{H O} \cdot (\text{C}_{32} \text{H}_{33})^{\sim} \text{C}_2, \text{O}_2 + \text{H O} \cdot (\text{C}_{32} \text{H}_{33})^{\sim} \text{C}_2, \text{O}_3$ —as:





I shall presently endeavour to establish the view that in a similar manner, sulphobenzoic, and sulphacetic acids are double acids, and owe their bibasic property to this circumstance.

According to the above hypothesis, the composition of the fatty acids would be expressed by the following rational formulæ :

HO .	H	---C <sub>2</sub> , O <sub>3</sub>	Formic acid.
HO .	(C <sub>2</sub> H <sub>3</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Acetic acid.
HO .	(C <sub>4</sub> H <sub>5</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Propionic acid.
HO .	(C <sub>6</sub> H <sub>7</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Butyric acid.
HO .	(C <sub>8</sub> H <sub>9</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Valeric acid.
HO .	(C <sub>10</sub> H <sub>11</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Caproic acid.
HO .	(C <sub>12</sub> H <sub>13</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Enanthylic acid.
HO .	(C <sub>14</sub> H <sub>15</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Caprylic acid.
HO .	(C <sub>16</sub> H <sub>17</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Pelargonic acid.
HO .	(C <sub>18</sub> H <sub>19</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Caprinic acid.
HO .	(C <sub>20</sub> H <sub>21</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Ricinostearic acid (margaritic acid).
HO .	(C <sub>22</sub> H <sub>23</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Laurostearic acid (pichurimo-stearic acid).
HO .	(C <sub>24</sub> H <sub>25</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Cocinic acid.
HO .	(C <sub>26</sub> H <sub>27</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Myristic acid.
HO .	(C <sub>28</sub> H <sub>29</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Benic acid.
HO .	(C <sub>30</sub> H <sub>31</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Æthalic acid.
HO .	(C <sub>32</sub> H <sub>33</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Margaric acid.
2HO .	{ (C <sub>32</sub> H <sub>33</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Stearic acid.
	{ (C <sub>32</sub> H <sub>33</sub> )	---C <sub>2</sub> , O <sub>3</sub>	
HO .	(C <sub>34</sub> H <sub>35</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Bassic acid.
HO .	(C <sub>42</sub> H <sub>43</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Behenic acid.
HO .	(C <sub>52</sub> H <sub>53</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Cerotic acid.
HO .	(C <sub>58</sub> H <sub>59</sub> )	---C <sub>2</sub> , O <sub>3</sub>	Melissic acid.

A glance at the above table will show that the radicals of the fatty acids contain, as adjuncts, the radicals of the alcohols, of which, however, we are as yet acquainted with only a few, namely, methyl, ethyl, amyl, cetyl, and cerotyl. The important discovery made by Dumas, that the ammonia-salts of acetic, propionic, valeric, and other acids, may, in accordance with the deportment of formiate of ammonia, be converted, by distillation with phosphoric acid for instance, into the cyanogen-compounds of the adjuncts of these acids—for instance, cyanide of methyl, cyanide of ethyl, cyanide of propyl, and cyanide of butyl—furnishes us with the prospect of obtaining by this method the whole series of alcohols that are

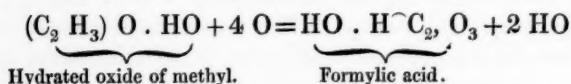
still wanting, provided we are successful in converting the cyanides into other combinations of the alcohol-radicals. The experiments hitherto made on this subject have, however, given no results.

Among the radicals of the fatty acids, formyl  $\text{H}^\cdot\text{C}_2$  stands to a certain extent isolated, it being the only one in which the adjunct contains no carbon. As, however, its compounds bear the greatest resemblance to those of acetyl, this would appear to indicate that the nature of the adjuncts of conjugate radicals exercises comparatively little influence over the chemical character of their compounds.

The composition of those formyl-compounds, of which the constitution is established with tolerable certainty, may be expressed by the following rational formulæ :

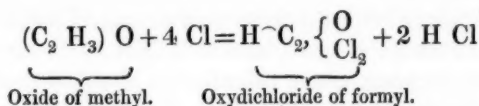
Formylic acid . . .	$\text{HO} \cdot \text{H}^\cdot\text{C}_2, \text{O}_2$	Formic acid.
Terchloride of formyl . .	$\text{H}^\cdot\text{C}_2, \text{Cl}_3$	Chloroform.
Terbromide of formyl . .	$\text{H}^\cdot\text{C}_2, \text{Br}_3$	Bromoform.
Teriodide of formyl . .	$\text{H}^\cdot\text{C}_2, \text{I}_3$	Iodoform.
Tersulphide of formyl . .	$\text{H}^\cdot\text{C}_2, \text{S}_3$	Sulphoform.
Dichloriodide of formyl .	$\text{H}^\cdot\text{C}_2, \left\{ \begin{array}{l} \text{Cl}_2 \\ \text{I} \end{array} \right.$	Chloriodoform.
Dibromoioidide of formyl .	$\text{H}^\cdot\text{C}_2, \left\{ \begin{array}{l} \text{Br}_3 \\ \text{I} \end{array} \right.$	Bromiodoform.
Diodocyanide of formyl .	$\text{H}^\cdot\text{C}_2, \left\{ \begin{array}{l} \text{I}_2 \\ \text{Cy} \end{array} \right.$	
Oxydichloride of formyl .	$\text{H}^\cdot\text{C}_2, \left\{ \begin{array}{l} \text{O} \\ \text{Cl}_2 \end{array} \right.$	Formyl-aci-bichloride (Berzelius). (Ether methylique bichloruré).

The analogy of hydrated oxide of methyl to hydrated oxide of ethyl, warrants the supposition that the former, in its oxidation and conversion into formic acid, undergoes a decomposition similar to that of the latter in its transformation into acetic acid ; namely, that the elimination of  $\text{C}_2 \text{H}_2$  from the composition of methyl, precedes the production of formic acid from methyl-alcohol :

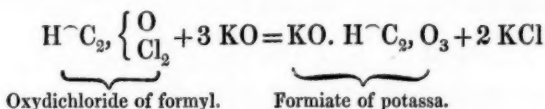


In the same manner, the rational formula  $\text{H}^\cdot\text{C}_2, \left\{ \begin{array}{l} \text{O} \\ \text{Cl}_2 \end{array} \right.$  for dichlorinated oxide of methyl, is based upon the supposition that when two equivalents of chlorine enter oxide of methyl in the place of two of hydrogen, it undergoes a metamorphosis correspond-

ing to the conversion of oxide of ethyl into oxydichloride of acetyl, namely :



Unfortunately, the chemical deportment of dichlorinated oxide of mythyl has been too little studied to admit of the deduction of any argument therefrom, for or against the above view ; it can only be supposed, from its analogy with dichlorinated oxide of ethyl (oxydichloride of acetyl), that alcoholic potassa would convert it into formic acid and hydrochloric acid :



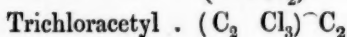
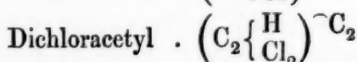
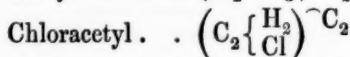
The view that the so-called perchlorinated ether, the pentachlorinated oxide of ethyl, no longer possessed the constitution of oxide of ethyl, was already defended, in opposition to the older theory of substitution, by Malaguti, in his excellent researches on the chlorinated ethers. Moreover, if we consider it established that chlorine, like oxygen, is capable of converting oxide of ethyl into an acetyl-compound, the pentachlorinated ether cannot really be a direct product of decomposition, and much less a substitution-product of oxide of ethyl, but must rather be considered as a derivative of oxydichloride of acetyl. Indeed, its most intimate relation to the acetyl-compounds may be inferred from its chemical comportment, and that of its products of decomposition, chloracetic acid, the so-called chloraldehyde, &c. Even the fact that perchlorinated ether, chloracetic acid, chloraldehyde, chloroxethose, &c., may be almost directly converted into acetic acid, and the latter again into chloracetic acid, renders it more than probable that all these bodies have a similar chemical constitution.

It becomes most clearly perceptible in the study of these compounds, into what a labyrinth of hypotheses, and to what very improbable assumptions we are forced, if we forsake, on the one hand, the theory of radicals, and adhere, on the other, to the immutability of organic radicals. It is certainly quite as difficult to agree with the hypotheses of Laurent and Dumas, as to adopt the views taken by Berzelius\* of the constitution of perchlorinated

\* Lehrbuch, 5th Edit. Vol. V. 788—825.

ether and its derivatives, and of the substitution-products of the ethers in general.

I will endeavour to interpret these phenomena of substitution from the point of view above adopted, and to base the following considerations upon the hypothesis, that a substitution of chlorine for hydrogen takes place in the acetyl-radical, without dissolving the complex atom, three new secondary radicals being produced thereby, which contain, in the place of one, two, or three equivalents of hydrogen, a proportionate number of equivalents of chlorine, and which are gifted with properties similar to those of acetyl itself. For the better indication of their relations to the latter, I will assign to them the names—chloracetyl, dichloracetyl, trichloracetyl, and express their rational composition by the following formulæ :

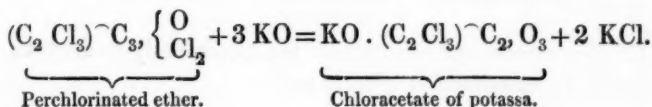


Of the various combinations of these three secondary acetyl-radicals, those of trichloracetyl have been by far the most accurately studied; I will therefore first submit them to examination.

Hydrated oxide of trichloracetyl	$\text{HO} \cdot (\text{C}_2 \text{ Cl}_3)^{\sim} \text{C}_2$	O	Chloral.
Trichloracetylic acid	$\text{HO} \cdot (\text{C}_2 \text{ Cl}_3)^{\sim} \text{C}_2$	O <sub>3</sub>	Chloracetic acid.
Oxide of trichloracetyl	$(\text{C}_2 \text{ Cl}_3)^{\sim} \text{C}_2$	O	Chloroxethose.
Chloride of trichloracetyl	$(\text{C}_2 \text{ Cl}_3)^{\sim} \text{C}_2$	Cl	Chlorethose (chlor. of carbon).
Oxydichloride of trichloracetyl	$(\text{C}_2 \text{ Cl}_3)^{\sim} \text{C}_2$	$\begin{cases} \text{O} \\ \text{Cl}_2 \end{cases}$	Chloride of chloroxethose.
Oxydibromide of trichloracetyl	$(\text{C}_2 \text{ Cl}_3)^{\sim} \text{C}_2$	$\begin{cases} \text{O} \\ \text{Br}_2 \end{cases}$	Bromide of chloroxethose.
Dinoxychloride of trichloracetyl	$(\text{C}_2 \text{ Cl}_3)^{\sim} \text{C}_2$	$\begin{cases} \text{O}_2 \\ \text{Cl} \end{cases}$	Chloraldehyde.
Dinoxamide of trichloracetyl	$(\text{C}_2 \text{ Cl}_3)^{\sim} \text{C}_2$	$\begin{cases} \text{O}_2 \\ \text{NH}_2 \end{cases}$	Chloracetamide.
Dinoxaphosphamide of trichloracetyl	$(\text{C}_2 \text{ Cl}_3)^{\sim} \text{C}_2$	$\begin{cases} \text{O}_2 \\ \text{PH}_2 \end{cases}$	Chloracetylphide.
Chlorodibromide of trichloracetyl	$(\text{C}_2 \text{ Cl}_3)^{\sim} \text{C}_2$	$\begin{cases} \text{Cl} \\ \text{Br}_2 \end{cases}$	Bromide of chlorethose.

We may easily perceive that those of the trichloracetyl-compounds above-mentioned, which are also represented in the acetyl-series, differ in various points in their properties and chemical comportment from the corresponding members of the latter series. The acetyl has evidently undergone no unimportant modifications by the exchange of its hydrogen for chlorine. In these instances, as in the substitution-products of aniline, the chlorine, to however great an extent it

appears to have lost its specific properties, imparts some portion of its chemical character to the combination in which it has entered the place of the hydrogen. This influence is rendered very distinctly evident in chloraniline and trichloraniline, by the weakening of the basic properties of the aniline; in the compounds of trichloracetyl it is not so obvious, although it is always rendered to a certain extent perceptible by a modification of the original affinities of acetyl. It should therefore not appear surprising, that chloracetic acid, when boiled, for instance, with potassa, deviates somewhat in its comportment from its analogue, acetic acid, or that oxydichloride of trichloracetyl (perchlorinated ether), the analogue of oxydichloride of acetyl (dichlorinated oxide of ethyl), should be decomposed with much greater difficulty, by similar treatment with potassa, than the latter. It is worthy of note, that the conversion of the chlorides (oxychlorides) of acetyl and trichloracetyl into the corresponding acids, is effected with greater ease, in proportion to the number of atoms of oxygen that the compound contains. While the terechloride of acetyl, which contains no oxygen, is but very slowly converted into acetic acid by boiling with alcoholic potassa, the oxydichloride of acetyl is converted into that acid with the greatest ease, by the mere action of water; and doubtless the dinoxychloride of acetyl, which is, as yet, unknown, but the production of which may be expected, with tolerable certainty, to result from the treatment of concentrated acetic acid with pentachloride of phosphorus, will be a liquid much more easily decomposed by water. On the other hand, dinoxychloride of trichloracetyl (chloraldehyde) is equally distinguished from the oxydichloride of trichloracetyl, by the facility with which it is converted into chloracetic acid.—Malaguti\* has left it undecided whether the small quantity of formic acid, which he detected in the fluid, after continuous boiling of perchlorinated ether with alcoholic potassa, owed its production to the action of the potassa on the alcohol, or to the conversion of perchlorinated ether into chloracetic acid:



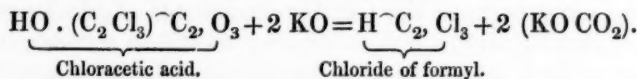
The simultaneous deposition of chloride of potassium gives, at any rate, a greater probability to the latter view.

The accompanying equations will show that, by the assumption of

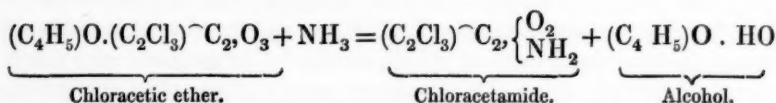
\* Ann. Ch. Phys. [3] XVI, 19.

a trichloracetyl, the most simple and natural explanations are furnished :

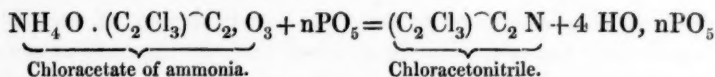
1. Of the decomposition of chloracetic acid into terchloride of formyl and carbonic acid by boiling with potassa :



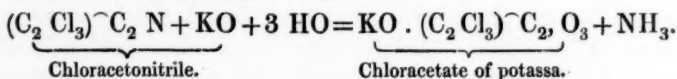
2. Of the formation of chloracetamide by the action of ammonia on chloracetate of oxide of ethyl :



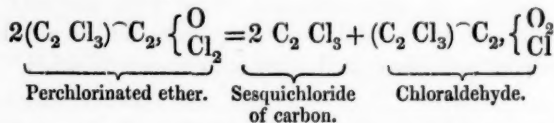
3. Of the conversion of chloracetate of ammonia by phosphoric acid into the substance, termed by its discoverers, Dumas, Malaguti, and Leblanc, chloracetoneitrile, and which is probably a cyanogen-compound  $(\text{C}_2 \text{Cl}_3) \cdot \text{C}_2 \text{N}$  :



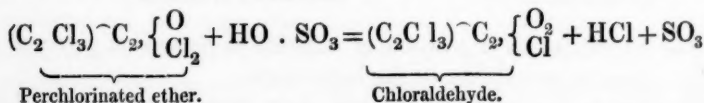
4. Of the reproduction of chloracetic acid and ammonia from chloracetoneitrile, by boiling with potassa :



5. Of the transformation of perchlorinated ether, at a temperature of  $300^\circ \text{C}$ ., into sesquichloride of carbon and dioxychloride of tri-chloracetyl (chloraldehyde) :

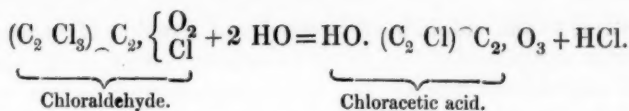


6. Of the metamorphosis which the latter body undergoes when heated with concentrated sulphuric acid :

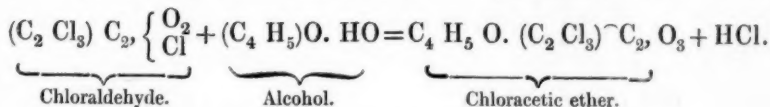


7. Of the decomposition of chloraldehyde by water into chloracetic acid and hydrochloric acid :

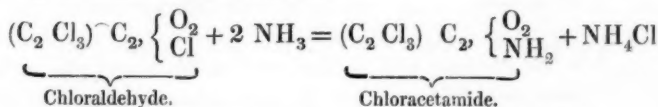




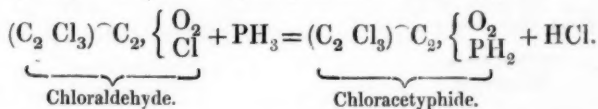
8. By alcohol into chloracetic ether and hydrochloric acid :



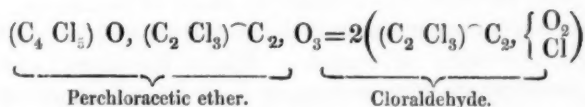
9. By ammonia into chloracetamide :



10. By terphosphide of hydrogen into chloracetyphide :

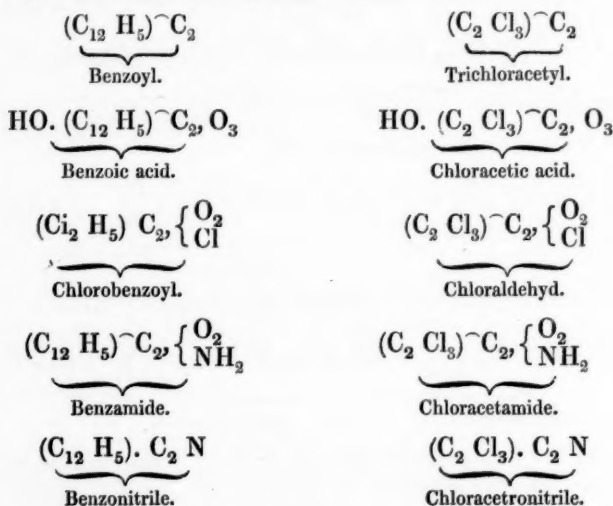


and finally, the formation of chloraldehyde by a simple change in the arrangement of the elements of the so-called perchloracetic ether, effected by passing the vapour of the latter through a dull, red-hot tube :

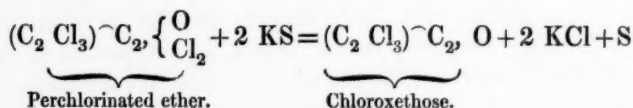


Chloraldehyde exhibits in its behaviour a remarkable similarity to the so-called chloride of benzoyl ( $C_{14} H_5 O_2 Cl$ ). The reason of this analogy between two such heterogeneous compounds may be easily arrived at, if the benzoyl-radical (free from oxygen) be viewed as a conjugate radical, like acetyl and trichloroacetyl, having the rational formula  $(C_{12} H_5)_C C_2$ . All three radicals possess in common the term  $C_2$ , forming the real point of attack for the powers of affinity of the negative elements, while the adjuncts alone are different. Here, then, the subordinate part played by the adjuncts compared with that of the body with which they are conjugated, and their comparatively slight influence over the chemical nature of the compounds of conjugate radicals, is again most strikingly exhibited. The above similarity is, however, not merely confined to chlorobenzoyl and chloraldehyde, it exists equally between benzoic acid and chloracetic acid, benzamide and chloracetamide, benzonitrile and chloracetonitrile, and will doubt-

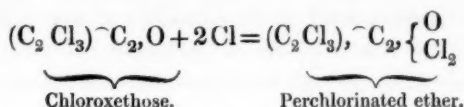
less extend to the sulphide of benzoyl and cyanide of benzoyl, and the terms corresponding in the trichloracetyl series, with which we are yet acquainted. The analogy of these compounds is best rendered evident by the following comparison of their rational formulæ :



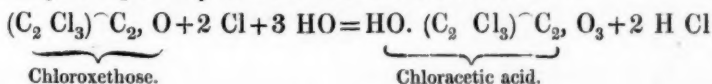
The difference between the behaviour of oxydichloride of trichloracetyl (perchlorinated ether) with sulphide of potassium, and that of the corresponding member of the acetyl series (the oxydichloride of acetyl), is worthy of remark. Whilst the latter, when treated with hydrosulphuric acid, exchanges 1 or 2 equivalents of chlorine for sulphur, the former undergoes a simple reduction, by treatment with an alcoholic solution of sulphide of potassium, and is converted into the oily compound called by Malaguti, chloroxethose ( $\text{C}_2 \text{Cl}_3\text{C}_2, \text{O}$  (oxide of trichloracetyl), sulphur and chloride of potassium being separated.



The mode of formation of chloroxethose, together with its property, when brought into contact with chlorine (or bromine), of combining directly with two equivalents of these elements, and thus being reconverted into perchlorinated ether (or the corresponding bromine-compound  $(\text{C}_2 \text{Cl}_3)\text{C}_2, \left\{ \begin{array}{l} \text{O} \\ \text{Br}_2 \end{array} \right.$  :



as also its comportment with chlorine in the presence of water, whereby it is partially converted into chloracetic acid :

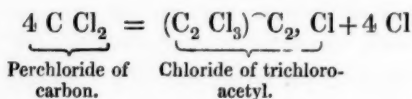


are in perfect accordance with the view expressed by the above formula, namely, that chloroxethose is the oxide of trichloracetyl.

The above considerations lead to the conjecture, by no means unfounded, that the chloride of carbon  $C Cl$  (Malaguti's chloride of chlorethose), which, in its comportment, exhibits so remarkable an analogy with oxide of trichloracetyl, is the chlorine-compound of the same radical, corresponding to this oxide, namely, chloride of trichloracetyl  $(C_2 Cl_3)^{\cdot}C_2 Cl$ . We may perhaps even go farther, and regard the sesquichloride of carbon, obtained from this chloride of trichloracetyl by direct assimilation of chlorine, as the higher chlorine-compound of the same radical, namely, as terchloride of trichloracetyl  $(C_2 Cl_3)^{\cdot}C_2 Cl_3$ , or at least assume the existence of two isomeric compounds,  $C_2 Cl_3$  (sesquichloride of carbon, trichloromethyl), and  $(C_2 Cl_3)^{\cdot}C_2 Cl_3$  (terchloride of trichloracetyl).

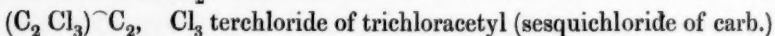
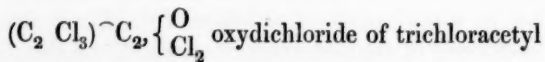
The principal objection against the assumption, that the chloride of carbon, produced by the combination of chloride of trichloracetyl with chlorine, is the terchloride of the latter radical, lies in the circumstance that we have not yet succeeded in replacing by oxygen the three equivalents of chlorine, considered as combined with trichloracetyl. Alcoholic solution of potassa is certainly not quite without action upon it, as, after continuous boiling, chloride of potassium is deposited, the liquid becoming brown ; neither chloracetic acid, terchloride of formyl, nor formic acid, can, however, be found among the products of decomposition. It is possible that in this experiment, the terchloride of trichloracetyl gives off two equivalents of chlorine to the potassium, without any replacement ensuing, the oxygen of the latter attacking the alcohol and oxidizing it to aldehyde ; this would also account for the brown colour assumed by the alcoholic potassa-solution. It must, however, be borne in mind, that terchloride of acetyl too is only attacked with difficulty by boiling alcoholic potassa, and that the action of the latter is likewise obstinately withstood by the oxydichloride of trichloracetyl. On the other hand, the conjecture that the so-called chloride and sesquichloride of carbon are chlorine-

compounds of trichloroacetyl, is supported by a vast number of facts. The formation of the chloride of trichloroacetyl from the so-called chloride of carbon, by passing the vapours of the latter through a red-hot tube :

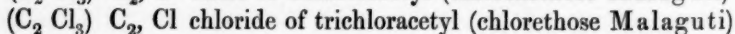
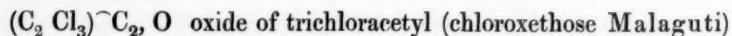


may be coupled with many similar examples, in which compounds poor in carbon, yield, by the action of a high temperature, less volatile substances richer in carbon, as, for instance, the formation of naphthalin, benzol, &c. The solid chloride, obtained together with the chloride of trichloroacetyl, doubtless owes its production to the further action of the large quantity of liberated chlorine upon the liquid chloride, and must therefore be considered as a secondary product of decomposition of the dichloride of carbon.

The remarkable similarity exhibited between the so-called sesquichloride of carbon and the oxydichloride of trichloroacetyl (perchlorinated ether) in their outward appearance, as also in their behaviour with hydrosulphate of potassium, a point to which attention was first called by Malaguti, finds a surprisingly simple explanation in the assumption of the rational formulæ  $(\text{C}_2 \text{ Cl}_3)_2 \text{ C}_2, \text{ Cl}_3$ , for the first named body. A simple comparison of the rational formulæ of these two substances :

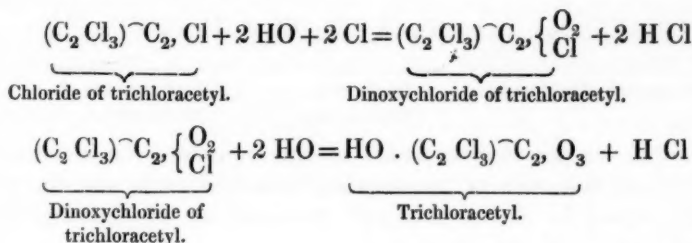


and of the corresponding members of the trichloroacetyl-series that are poorer in chlorine, namely, of oxide of trichloroacetyl and chloride of trichloroacetyl :



is only needed to account for the concordant behaviour of the two former compounds with hydrosulphate of sulphide of potassium, and of the two latter with chlorine and bromine, and particularly to explain the remarkable relations of the two latter to chloroacetic acid. With regard to the transformation of chloride of trichloroacetyl into chloroacetic acid, by exposure to the action of chlorine in the presence of water, under the influence of solar light, it is partly due to the decomposition of water into hydrochloric acid and oxygen, and partly

to the power possessed by chloride of trichloracetyl, of combining with oxygen directly, as it does with chlorine, at least when the former is in the nascent state. Dinooxychloride of trichloracetyl (chloraldehyde) is next formed, and this, being readily decomposed by water, is converted into chloracetylic acid.



The conversion of the greater part of the chloride of trichloracetyl into terchloride of trichloracetyl, in the above process, is doubtless owing to the slowness with which the oxygen is liberated from water by the chlorine.

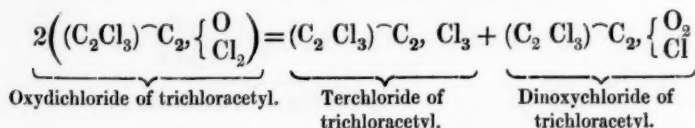
If a similar condensation of the elements be assumed in trichloracetyl as in acetyl, one volume of trichloracetyl, containing therefore two volumes of carbon-vapour and three volumes of chlorine ;

2 vol. carbon-vapour . . .	1·658
3 „ chlorine . . . . .	7·346
1 vol. trichloracetyl . . .	9·004

and if the chloride of trichloracetyl and terchloride of trichloracetyl be regarded as containing, according to the usual modes of condensation, half a volume of trichloracetyl, combined respectively with half a volume or one and a half volume of chlorine, the calculation of the specific gravities of these bodies in the gaseous form, will furnish numbers, corresponding very closely with the observed vapour densities of the so-called protochloride of carbon = 5·82 and sesquichloride of carbon = 8·157 :

$\frac{1}{2}$ vol. trichloracetyl . . . . .	4·502
$\frac{1}{2}$ „ chlorine . . . . .	1·224
1 vol. chloride of trichloracetyl . . .	5·726
$\frac{1}{2}$ vol. trichloracetyl . . . . .	4·502
$\frac{3}{2}$ „ chlorine . . . . .	3·672
1 vol. terchloride of trichloracetyl . .	8·174

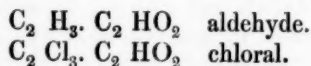
It is worth mentioning here, that the decomposition of oxydichloride of trichloracetyl into two equivalents of sesquichloride of carbon, and one equivalent of dinoxychloride of trichloracetyl, at a temperature of 300° C., may be even more simply expressed by the following equation, than by the mode of viewing adopted at page 384 :



According to the view expressed in this equation, the metamorphosis of oxydichloride of trichloracetyl into terchloride and dinoxychloride, would be due to a simple transposition of the negative elements combined with the radical.

The remaining modes of formation of the chloride of trichloracetyl, for instance, by the action of chlorine on chloride of ethyl and hydrochlorate of chloride of vinyl (oil of olefant gas), appear to me to accord likewise with the above assumption ; in the first case, the terchloride of trichloracetyl is not formed as a direct product of decomposition of chloride of ethyl, but as a substitution-product of the terchloride of acetyl, into which the chloride of ethyl is first converted ; in the second case, the formation of the terchloride is evidently preceded by that of the chloride of trichloracetyl, which may again be viewed as a product of decomposition of the hydrochlorate of chloride of trichlorovinyl  $(\text{C}_4\text{Cl}_3)\text{Cl}$ .  $\text{HCl}$ , lately discovered by Pierre, from which it is probably produced, in consequence of the separation of the apparently but loosely combined hydrochloric acid, by the transposition of the elements from  $(\text{C}_4\text{Cl}_3)\text{Cl}$  into  $(\text{C}_2\text{Cl}_3)\text{C}_2, \text{Cl}$ . (Compare the note, page 376.)

In speaking, some time back, of the chemical constitution of aldehyde and chloral,\* I advanced the assumption that they might be conjugate combinations of formylous acid respectively with methyl and sesquichloride of carbon :

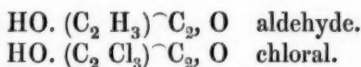


According to this view, by which the close relations of these two compounds is very well expressed, and a satisfactory interpretation given of the decomposition of chloral by alkalis into terchloride of

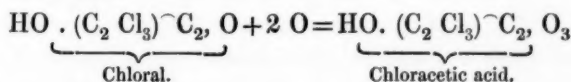
\* Ann. Chem. Pharm. LIV, 184.



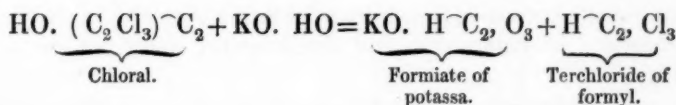
formyl and formic acid, the oxidation, in the conversion of aldehyde into acetic, and of chloral into chloracetic acid, would extend to the common constituent, formylous acid, which would be transformed into conjugate oxalic acid, with formation of water. If, however, the readiness with which the elimination of hydrogen-equivalents proceeds, at least in aldehyde, be taken into consideration, it must appear strange that the action of chlorine should confine itself solely to the hydrogen of the adjunct, and that the formylous acid, so readily acted upon by oxygen, should remain unaltered. This difficulty is immediately overruled, by assuming, with Liebig, the pre-existence of a basic atom of water in chloral as well as in aldehyde, and by viewing the former as hydrated oxide of acetyl, and the latter as hydrated oxide of trichloracetyl :



The formation of chloracetic acid, in the oxidation of chloral by means of fuming nitric acid, would then be, as in the conversion of aldehyde into acetic acid, the result of the direct assumption of two equivalents of oxygen :



This hypothesis likewise furnishes a proper explanation of the decomposition of chloral, by solution of potassa, into formic acid and terchloride of formyl, as is shown by the following equation :

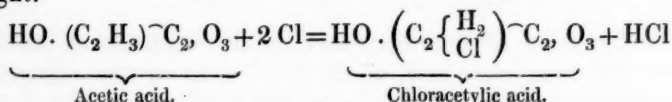


With regard to the interesting metamorphosis which hydrate of chloral undergoes by treatment with sulphuric acid, other expressions may be easily given of the composition of chloralide, accounting equally well for its formation and chemical comportment as the formula  $2 \text{C}_2 \text{HCl}_3 \cdot 3 \text{C}_2 \text{O}_2$  constructed by Städelcr,\* which it is difficult to bring into accordance with the above view of the constitution of chloral. It might, with equal justice, be considered as a combination of two equivalents of oxide of trichloracetyl with one equivalent of hydrate of formic acid  $= 2 [(\text{C}_2 \text{Cl}_3 \cdot \text{C}_2, \text{O})] + \text{HO. HC}_2, \text{O}_3$ , or as a double

\* Ann. Ch. Pharm. LXI, 104.

compound of chloral and formiate of the oxide of trichloracetyl =  $\text{HO} \cdot (\text{C}_2 \text{Cl}_3) \cdot \text{C}_2, \text{O} + (\text{C}_2 \text{H}_3) \cdot \text{C}_2, \text{O} \cdot \text{H} \cdot \text{C}_2, \text{O}_3$ . It is left for future researches to decide which of these formulæ can claim the advantage, or which view of the rational composition of chloralide is the correct one.

It has already been stated that we are as yet only acquainted with a few compounds of the intermediate secondary acetyl-radicals preceding trichloracetyl, namely, chloracetyl  $(\text{C}_2 \{ \frac{\text{H}_2}{\text{Cl}} \}) \cdot \text{C}_2$ , and dichloracetyl  $(\text{C}_2 \{ \frac{\text{H}}{\text{Cl}_2} \}) \cdot \text{C}_2$ . One of the most interesting is the acid of chloracetyl, corresponding to that of trichloracetyl, namely, chloracetylic acid  $\text{HO} \cdot (\text{C}_2 \{ \frac{\text{H}_2}{\text{Cl}} \}) \cdot \text{C}_2, \text{O}_3$ , which Leblanc\* prepared by the action of dry chlorine-gas on concentrated acetic acid in diffused daylight.



We must also include, among these bodies, the two substitution-products of terchloride of acetyl, described by Regnault,† and resulting, together with chloride of acetyl, from the decomposition of the so-called chloride of aldehyde (first substitution-product of chloride of ethyl), namely, the terchloride of chloracetyl  $(\text{C}_2 \{ \frac{\text{H}_2}{\text{Cl}} \}) \cdot \text{C}_3, \text{Cl}_3$ , (trichlorinated chloride of ethyl), and terchloride of dichloracetyl  $(\text{C}_2 \{ \frac{\text{H}}{\text{Cl}_2} \}) \cdot \text{C}_2, \text{Cl}_3$  (tetrachlorinated chloride of ethyl.) The substitution-products corresponding to oxydichloride of acetyl, namely, the oxydichlorides of chloracetyl and dichloracetyl, have not yet been obtained.

The vapour-densities of terchloride of acetyl (= 4·530), of terchloride of chloracetyl (= 5·799), of terchloride of dichloracetyl (= 6·983), and terchloride of trichloracetyl (= 8·157), as determined by Regnault, are in perfect accordance with the above assumption, if we consider  $\frac{1}{2}$  vol. of each of the radicals of these bodies combined with  $\frac{3}{2}$  vol. of chlorine to form 1 volume, according to the usual mode of condensation.

Acetyl $(\text{C}_2 \text{H}_3) \cdot \text{C}_2$ .		Terchloride of acetyl $(\text{C}_2 \text{H}_3) \cdot \text{C}_2, \text{Cl}_3$ .	
2 vols. carbon vapour.	1·658	$\frac{1}{2}$ vol. acetyl gas . . .	0·932
3 „ hydrogen . . .	0·207	$\frac{3}{2}$ „ chlorine . . .	3·604
1 vol. acetyl . . .	1·865	1 vol. terchloride of acetyl.	4·536
		(found . . .)	4·530

\* Ann. Chim. Phys. [3] LXXI, 353.

† Ibid, X. 212.

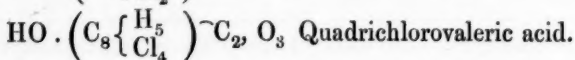
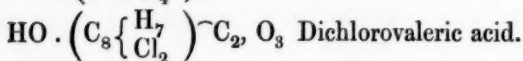
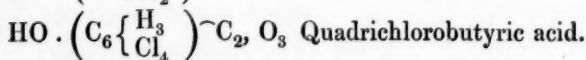
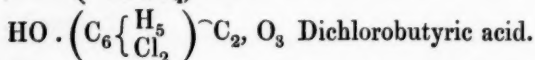
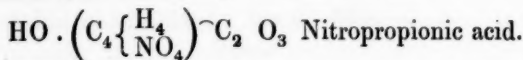
Chloracetyl $(C_2 \{ \frac{H_2}{Cl} \})^- C_2$		Terehloride of chloracetyl $(C_2 \{ \frac{H}{Cl} \})^- C_2O, Cl_3$	
2 vols. carbon-vapour.	1·658	$\frac{1}{2}$ vol. chloracetyl-gas	2·123
2 „ hydrogen	0·138	$\frac{3}{2}$ „ chlorine	3·672
1 vol. chlorine	2·449		
1 vol. chloracetyl	4·247	1 vol. terehloride of chloracetyl	5·795 (found . 5·799)
Dichloracetyl $(C_2 \{ \frac{H_2}{Cl} \})^- C_2$		Chloride of dichloracetyl : $(C_2 \{ \frac{H}{Cl_3} \})^- C_2, C$	
2 vols. carbon-vapour	1·658	$\frac{1}{2}$ vol. dichloracetyl-gas	3·314
1 „ hydrogen	0·069	$\frac{3}{2}$ „ chlorine	3·672
2 „ chlorine	4·898		
1 vol. dichloracetyl	6·628	1 vol. chlor. of dichloracetyl	6·986 (found . 6·983)
Trichloracetyl $(C_2 Cl_3)^- C_2$		Chloride of trichloracetyl $(C_2 Cl_3)^- C_2, Cl_3$	
2 vols. carbon-vapour	1·658	$\frac{1}{2}$ vol. trichloracetyl-gas	4·502
3 „ chlorine	7·346	$\frac{3}{2}$ „ chlorine	3·672
1 vol. trichloracetyl	9·004	1 vol. chlor. of trichloracetyl	8·174 (found . 8·157)

The metamorphoses which chloride of ethyl undergoes consecutively by the action of chlorine, may be exhibited by the following formulæ of the resulting products of decomposition :

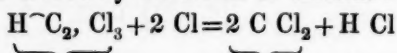
Protochloride of ethyl	$(C_4 H_5) Cl$	éther hydrochlorique
Hydrochlorate of protochloride of acetyl	$(C_2 H_3)^- C_2, Cl, HCl$	{ éther hydrochlor. monochloruré.
Terehloride of acetyl	$(C_2 H_3)^- C_2, Cl_3$	{ éther hydrochlor. bichloruré.
Terehloride of chloracetyl	$(C_2 \{ \frac{H_3}{Cl} \})^- C_2, Cl_3$	{ éther hydrochlor. trichloruré.
Terehloride of dichloracetyl	$(C_2 \{ \frac{H_3}{Cl_2} \})^- C_2, Cl_3$	{ éther hydrochlor. quadrichloruré.
Terehloride of trichloracetyl	$(C_2 Cl_3)^- C_2, Cl_3$	{ éther hydrochlor. perchloruré.

It still remains for us to discuss the chemical constitution of those bodies, which are produced by substitution from the combinations of the other radicals homologous with acetyl. With regard to chlorobutyric and chlorovaleric acid, as also to nitropropionic acid, the assumption of the conjugate radicals  $(C_4 H_5)^- C_2$ ,  $(C_6 H_7)^- C_2$ , and  $(C_8 H_9)^- C_2$  in propionic, butyric, and valeric acids, and the analogy of these substances with acetic acid, scarcely admit any other explanation of the above processes of substitution than that the

hydrogen in the adjuncts of these radicals is substituted by chlorine, hyponitric acid, &c., new secondary radicals being thus produced, which still possess the constitution of the primary radicals. Hence, the composition of nitropropionic, chlorobutyric, and chlorovaleric acids, is expressed by the following rational formulæ.



It is much more difficult to explain satisfactorily the metamorphoses which the formyl-compounds undergo by the action of chlorine. Although I do not dispute the existence of a secondary formyl-radical of the composition  $\text{Cl} \cdot \text{C}_2$ , but am, on the contrary, convinced of its existence in chlorinated formiate of oxide of ethyl, and of oxide of methyl, yet the assumption of its existence in the substitution-products of the simple formyl-compounds, for instance, in chlorinated chloride of formyl, oxydichloride of formyl, &c., appears to me exceedingly bold and improbable. Even the behaviour of hydrated formic acid with chlorine, by which it is converted not into chloroformic ( $\text{HO} \cdot \text{Cl} \cdot \text{C}_2 \text{O}_3$ ), but into hydrochloric and carbonic acids, unmistakeably indicates the action of affinities different from those exerted in compounds, the radicals of which contain a carbohydrogen as adjunct. Terechloride of formyl undergoes an analogous decomposition, being split up, as is well known, into two equivalents of perchloride of carbon by the action of chlorine :



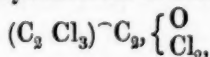
Terechloride of formyl. Perchloride of carbon.

It would at any rate be difficult to deduce from the chemical comportment of perchloride of carbon, any argument in favour of that substance being terechloride of chloroformyl ( $\text{Cl} \cdot \text{C}_2, \text{Cl}_3$ ), or chloride of trichloromethyl ( $\text{C}_2 \text{Cl}_3, \text{Cl}$ ), or of its possessing any other rational formula.—The chlorinated oxydichloride of formyl (the final product of the action of chlorine on oxide of methyl, having the empirical formula  $\text{C}_2 \text{Cl}_3 \text{O}$ ), has been unfortunately too little studied to afford, by its comportment, any conclusion as to its constitution. It may, perhaps,

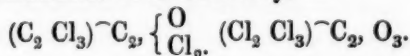
be a simple combination of perchloride of carbon with chloro-carbonic acid, having the rational formula  $C Cl_2, C \begin{Bmatrix} O \\ Cl \end{Bmatrix}$ . This product appears at any rate no longer to possess the constitution of oxide of methyl, nor of oxybichloride of formyl; at least, the observation made by Regnault, that the condensation of the so-called oxide of perchloro-methyl in the gaseous form is only half as great as that of the compound from which it is directly derived, appears to indicate that the conversion of oxydichloride of formyl (dichlorinated oxide of methyl) into oxide of perchloromethyl is accompanied by a change in the relative position of the atoms.

It is at present impossible to decide whether the final product of the action of chlorine on sulphide of methyl is analogous in composition to the foregoing substance, or whether its composition may be expressed by the rational formula  $C Cl_2, C \begin{Bmatrix} S \\ Cl \end{Bmatrix}$ .

Malaguti,\* in his admirable researches on the chlorinated ethers, was the first to advance, and support with powerful arguments, the view that the various compound chlorinated ethers examined by him (in which all the hydrogen was substituted by chlorine), contain no perchlorinated ether, in the form in which it is known in the isolated state (oxydichloride of trichloroacetyl), but that they more probably have the same constitution as the normal ethers of which they are the derivatives. The composition of perchloroacetic ether would then be expressed by the rational formula  $(C_4 Cl_5) O, (C_2 Cl_3)^- C_2, O_3$ . If it were assumed, on the other hand, that the oxide of ethyl, in acetic ether, in its conversion into perchloroacetic ether underwent the same metamorphosis as it does in the free state, namely, that it was converted thereby into oxydichloride of trichloroacetyl



the perchloroacetic ether would then have to be viewed as trichloroacetate of oxydichloride of trichloroacetyl =



Irrespective of the arguments maintained by Malaguti against the existence of perchlorinated ether, as it is known in the free state, in perchloroacetic ether, it appears to me in itself but slightly probable that, in a metamorphosis so completely altering the molecular arrangement of atoms, as, for instance, in the conversion of carbonate of oxide of ethyl  $(C_4 H_5) O, CO_3$ , into carbonate of oxydichloride of

\* Ann. Chem Phys. [3] XVI, 4.

trichloracetyl  $(C_2 Cl_3)^-C_2 \cdot \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right. CO_2$ , the two members—carbonic acid and oxydichloride of trichloracetyl should remain combined. The objection may be raised here, that it is still enigmatical why the action of chlorine on oxide of ethyl, combined with acids, produces no change in the molecular arrangement of the atoms, while free oxide of ethyl, under similar circumstances, immediately passes into an acetyl-compound; this may be answered by referring to the many cases in which a compound owes its existence solely to its combination with another body, or even to the mere presence of such a substance. Carbamic acid, cyanic acid, and many others, are well known to exist only in combination with bases; they split up on the moment of their liberation into simpler groups of atoms. We know, likewise, that the addition of a few drops of solution of potassa to the neutral aqueous solution of a large quantity of sulphovinate of potassa, is sufficient to prevent perfectly the easy decomposition of that substance by boiling. If, moreover, the view be adopted without hesitation, that in hyposulphobenzolic and naphthalic acids, the hyposulphuric acid assumed as existing therein, acquires a stability perfectly foreign to it when in the free state, by the assimilation of the adjunct, it is certainly not less justifiable to assume that the elements of oxide of ethyl in compound ethers, are held together with a greater force, by their combination with acids, than is the case with free oxide of ethyl, so that the original grouping of atoms remains the same, even if chlorine be replaced for all the hydrogen-equivalents of a compound ether. The property possessed by so many binary compounds, of gaining increased stability by their combination with a third body, may be compared to the action of a powerful magnet on two weaker ones, which alone have not power sufficient to support each other, but to which this power is imparted on the approach of a more powerful magnet.

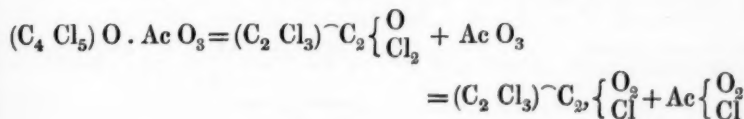
It must not, however, be considered strange that we have not as yet succeeded, and perhaps never shall be successful, in converting the chlorinated compound ethers into the normal ethers by a process similar to that by which chloracetic acid is reconverted into acetic acid, and chloraniline into aniline. The attachment of their constituents, the chlorinated acid and the chlorinated oxide of ethyl, appears weakened to such a degree by the entrance of chlorine in the place of hydrogen, that a comparatively slight impulse, such as is imparted by the action of heat, alkalis, alcohol, &c., is required to effect an essential change in the molecular arrangement of their atoms. All the endeavours to reproduce the original compounds



from the chlorinated ethers have met with no result, and it is probable that the slight stability of the latter compounds will always present an insurmountable obstacle to the success of such experiments.

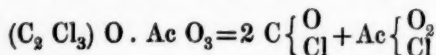
The highly interesting and numerous metamorphoses of chlorinated compound ethers, for the knowledge of which we are principally indebted to Malaguti and Cahours, furnish undoubtedly the most appropriate means of deciding the question of the rational composition of the latter substances. We will therefore examine the explanation furnished of these phenomena, by the above mode of viewing.

The metamorphoses of the various chlorinated ethers containing chlorinated oxide of ethyl, by potassa, ammonia, alcohol, methyl-alcohol, &c., exhibit a remarkable analogy in the circumstance that the resulting products of decomposition are the same as would be furnished by a combination, or a mixture, of the particular (chlorinated) acid with dinoxychloride of trichloracetyl (chloraldehyde). It may hence be assumed with tolerable certainty that the contact of these substances with the above agents, always effects, in the first instance, their separation into the two groups of atoms composing them, namely, into chlorinated oxide of ethyl and the chlorinated acid. It appears, however, that a chlorinated oxide of ethyl cannot exist as such, but exhibits a tendency to pass over into the metamerie compound, oxydichloride of trichloracetyl  $(C_2 Cl)_2 C_2 \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$ , while the acids, separated from chlorinated oxide of ethyl (with the exception of carbonic acid), cannot exist in the anhydrous state. It is therefore probable that, at the moment of separation, an exchange is effected of one equivalent of oxygen for one of chlorine in the chlorinated oxide of ethyl, while it undergoes the above metamorphosis; whereby there is formed, on the one hand, an oxychloride corresponding to the hypothetically anhydrous acid, or a direct product of decomposition, produced by a transposition of the atoms, and, on the other hand, dinoxychloride of trichloracetyl. This metamorphosis may be best understood by means of the following general equation, in which Ac represents the acid-radical :

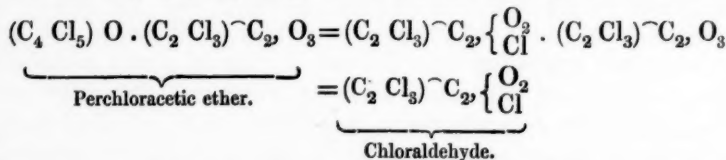


Indeed, the term  $(C_2 Cl_3)_2 C_2 \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right.$  (the so-called chloraldehyde) is found to be a constant product of decomposition, by heat, of all com-

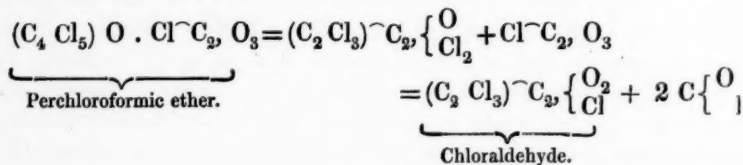
pound ethers containing chlorinated oxide of ethyl, accompanied by a compound corresponding in composition to the formula  $\text{Ac} \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix} \right\}$  or at least by a direct product of decomposition of the latter. The chlorinated ethers of oxide of methyl undergo a perfectly analogous metamorphosis, with the only difference that, in this case, chlorocarbonic acid is formed, instead of  $(\text{C}_2 \text{Cl}_3)^{\sim} \text{C}_2, \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix} \right\}$ :



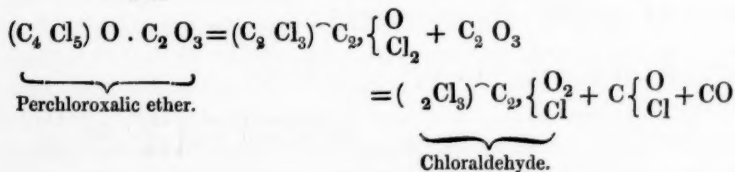
The above rationale holds good likewise with respect to the conversion of perchloracetic ether into two equivalents of the dinoxychloride of trichloroacetyl (chloraldehyde), having the same composition as the former, by the passage of its vapours through a red-hot tube:



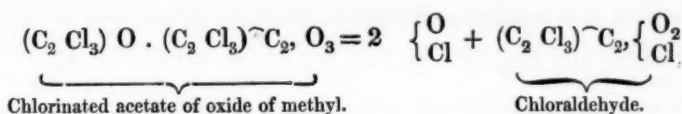
the decomposition of chlorinated formate of oxide of ethyl into chloraldehyde and chloracarbonic acid:



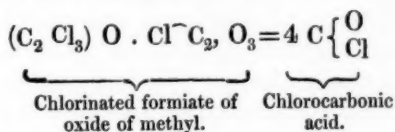
that of perchloroxalic ether into chloraldehyde, chlorocarbonic acid and carbonic oxide (the two latter being doubtless products of decomposition of  $\text{C}_2 \left\{ \begin{smallmatrix} \text{O}_2 \\ \text{Cl} \end{smallmatrix} \right\}$  (still unknown) :



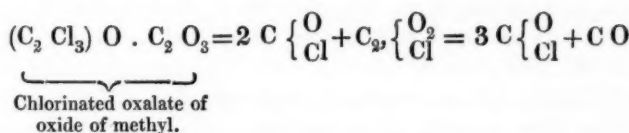
as also with the decomposition of the perchlorinated acetate of oxide of methyl, isomeric with perchloroformic ether, into chlorocarbonic acid and chloraldehyde:



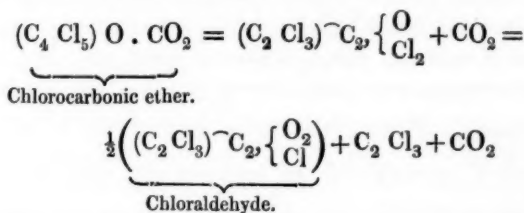
of chlorinated formiate of oxide of methyl into four equivalents of the isomeric compound, chlorocarbonic acid :



and of the chlorinated oxalate of oxide of methyl, into chlorocarbonic acid and carbonic oxide :



The metamorphosis of perchlorocarbonic ether, by exposure to heat, into chloraldehyde, sesquichloride of carbon, and carbonic acid,



exhibits a slight deviation from the above, which is evidently based, partly upon the property of carbonic acid of existing in the anhydrous state, and partly upon its volatility. The latter is probably the principal cause why the carbonic acid, at the moment that it should exchange an equivalent of oxygen for an equivalent of chlorine with the intermediate product, oxydichloride of trichloracetyl

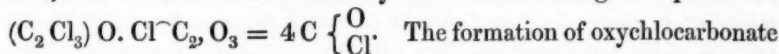
$(\text{C}_2 \text{Cl}_3)^{\sim} \text{C}_2, \left\{ \begin{array}{c} \text{O} \\ \text{Cl}_2 \end{array} \right\}$  (which is undergoing transposition), evades this metamorphosis, so that the latter substance alone undergoes a further change; and thus we obtain, instead of chloraldehyde and chlorocarbonic acid, carbonic acid and the products of decomposition of oxydichloride of trichloracetyl, namely, chloraldehyde and sesquichloride of carbon.

We find, in accordance with the above assumptions, that perchloracetic ether:  $(C_4 Cl_5) O \cdot (C_2 Cl_3)^- C_2, O_3 = 2 \left( C_2 Cl_3 \right)^- C_2, \left\{ \begin{smallmatrix} O_2 \\ Cl \end{smallmatrix} \right\}$  behaves with potassa, ammonia, and alcohol, exactly like dinoxychloride of trichloracetyl (chloraldehyde); potassa forming with it trichloracetate of potassa and chloride of potassium; ammonia: dinoxamide of trichloracetyl (chloracetamide) and chloride of ammonium; alcohol: trichloracetate of oxide of ethyl and hydrochloric acid.—In like manner, chlorinated formiate of oxide of ethyl and the metamerie acetate of oxide of methyl, behave with these reagents like a mixture of chlorocarbonic acid and chloraldehyde (compare their metamorphoses at a high temperature, p. 399). Solution of potassa converts them into trichloracetate and carbonate of potassa, and chloride of potassium; ammonia into chloracetamide and chloride of ammonium (and doubtless into carbamide or its products of decomposition); alcohol into trichloracetate and oxychlorocarbonate of oxide of ethyl and hydrochloric acid; methyl-alcohol into the corresponding methyl-ethers.—Chlorinated carbonate of oxide of ethyl, which is converted by potassa into chloride of potassium, carbonate and formiate of potassa (the latter being evidently a product of decomposition of the previously formed trichloracetate of potassa); by ammonia into chloride of ammonium, chloracetamide (and probably carbamide and carbamate of ammonia), and which furnishes, with alcohol, trichloracetate and carbonate of oxide of ethyl, besides hydrochloric acid, resembles in these metamorphoses an instable compound of chloraldehyde and chlorocarbonic acid:  $(C_4 Cl_5) O \cdot CO_2 = (C_2 Cl_3)^- C_2, \left\{ \begin{smallmatrix} O_2 \\ Cl \end{smallmatrix} \right\} + C \left\{ \begin{smallmatrix} O \\ Cl \end{smallmatrix} \right\}$  or a compound of oxydichloride of trichloracetyl with carbonic acid:  $(C_4 Cl_5) O, CO_2 = (C_2 Cl_3)^- C_2, \left\{ \begin{smallmatrix} O \\ Cl_2 \end{smallmatrix} \right\} \cdot CO_2$ , if we may assume that oxydichloride of trichloracetyl, at the moment of its formation, can pass over, with the elements of water, into trichloracetylic and hydrochloric acids, analogously to the dinoxychloride of trichloracetyl.—The chlorinated oxalate of oxide of ethyl, which yields with potassa: trichloracetate and oxalate of potassa and chloride of potassium; with ammonia: chloracetamide, chloride of ammonium, and probably oxamide; with alcohol: trichloracetate and oxalate of oxide of ethyl, together with hydrochloric acid and chloride of ethyl, comports itself like a compound of chloraldehyde with a hypothetical oxalo-dinoxychloride, corresponding to oxamide:  $C_2, \left\{ \begin{smallmatrix} O_2 \\ Cl \end{smallmatrix} \right\}$  which may be presumed to be decomposed by ammonia into chloride of ammonium and oxamide. In the decompo-

sition of chlorinated oxalate of oxide of ethyl by alcohol, Malaguti observed, besides the formation of oxalic ether and chloracetic ether, the production of the body  $C_8 Cl_5 O_7$  (Chloroxethide M), corresponding in composition to the formula  $(C_4 Cl_5) O \cdot 2 C_2 O_3$  (?).

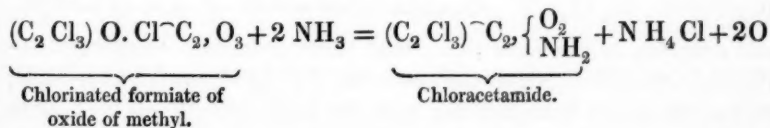
In the same manner, the decomposition of chlorinated oxalate of methyl by potassa into chloride of potassium, oxalate and carbonate of potassa,—by alcohol into hydrochloric acid, oxalate and chlorocarbonate of oxide of ethyl,—and by ammonia into chloride of ammonia and carbamide (and doubtless oxamide) corresponds perfectly with the comportment of a compound of chlorocarbonic acid with the above-mentioned hypothetical oxalo-dinoxylchloride.

It might be expected, from the analogy of chlorinated formiate of oxide of ethyl with the other compound chlorinated ethers, that it would comport itself with the above reagents, like chlorocarbonic acid, into which it is converted by the action of a high temperature :



of oxide of ethyl and hydrochloric acid by treatment of the chlorinated ether with alcohol, is likewise in accordance with this supposition; instead, however, of yielding chloride of ammonium and carbamide, by treatment with ammonia, it is stated by Cahours to yield dinoxamide of trichloracetyl (chloracetamide).

Although the percentage-composition obtained by Cahours for the latter compound agrees exactly with that of chloracetamide, I cannot refrain from doubting the above statement, and presuming that it must be based upon some error. Additional weight is given to this supposition by the fact that, in endeavouring to construct the formula of chloracetamide from that of the chlorinated formiate of oxide of methyl, there remain two atoms of oxygen, of the use of which no account can be rendered, as will be seen from the following equation :



It is very desirable that Cahours should repeat this experiment, and remove the doubts on the subject.

I shall refrain from making any observations on chlorosuccinic ether and its complicated decompositions, described by Malaguti, as it is my belief that the metamorphoses which free succinic acid undergoes by the action of chlorine, must be first examined and determined,

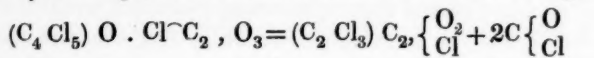
before we can furnish any account of the rational composition of chlorosuccinic ether, or of its products of decomposition.

The perfect similarity exhibited by chlorinated acetate of oxide of methyl and chlorinated formiate of oxide of ethyl, as far as our present knowledge of them extends, has induced most chemists to consider them as identical. While the most different views exist respecting the manner in which the elements are grouped in these two compounds, their supposed identity has been employed as an argument against the assertion, that compound chlorinated ethers still possess the constitution of the normal ethers. I myself am far from concluding that, because the chlorinated ethers, which have hitherto been more carefully examined, exhibit an analogy with those from which they have been produced,—the molecular arrangement of the atoms and of the proximate constituents must likewise remain unaltered in the action of chlorine on all other compound ethers; on the contrary, I consider it more than probable that ethers of complex composition, such as chlorinated amylic-ether, valerianic, or even margaric ethers, cease to possess the constitution of the original ethers long before the whole of the hydrogen is replaced by chlorine. Perhaps even the chlorinated succinic ether belongs to this class, as its complex composition and metamorphoses lead to the assumption that the exchange of its hydrogen for chlorine is followed by a far more intricate decomposition. The identity of chlorinated formiate of oxide of ethyl and chlorinated acetate of oxide of methyl, even if it were established, could therefore not serve absolutely to determine our views concerning the nature of other chlorinated ethers. But I am not of opinion that the two latter compounds have the same chemical constitution, and are really identical, because they are alike in their comportment. If we view these two others as composed according to the rational formulæ :

$(C_4 Cl_5) O \cdot Cl \cdot C_2, O_3$  chlorinated formiate of oxide of ethyl,

$(C_2 Cl_3) O \cdot (C_2 Cl_3) \cdot C_2, O_3$  chlorinated acetate of oxide of methyl,

and consider, at the same time, that their proximate constituents— $(C_4 Cl_5) O$  and  $Cl \cdot C_2, O_3$  on the one hand,  $(C_2 Cl_3) O$ , and  $(C_2 Cl_3) \cdot C_2, O_3$  on the other—are held together with but feeble affinity—if we bear in mind, moreover, that, as no one of these adjuncts exists in the uncombined state, at the moment that their chemical equilibrium is disturbed by the influence of any agent, their further decomposition must be preceded by a transposition of their atoms after the following manner :

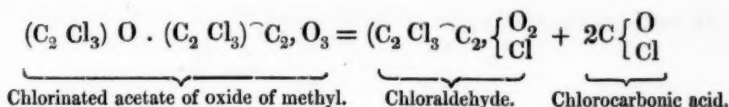


Chlorinated formiate of oxide  
of ethyl.

Chloraldehyde.

Chlorocarbonic  
acid.





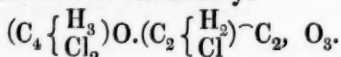
(these metamorphoses being produced in reality by the action of a high temperature);—if all these circumstances be duly considered, it will be easily understood why these two bodies exhibit a similar comportment, or, at any rate, yield the same products of decomposition with such agents as are capable of effecting this disturbance in the chemical equilibrium of their constituents. Their correspondence, besides, in specific gravity, boiling-point, &c., must, least of all, excite surprise, as even the two normal ethers, from which they are produced, exhibit a perfect similarity in these respects. Acetate of oxide of methyl and formiate of oxide of ethyl are well known to differ only in their behaviour when boiled with alkalis; they evidently owe this mark of distinction to the greater stability of their constituents, without which they would probably be likewise considered as identical. I feel convinced that, by a careful investigation and comparison of these two chlorinated ethers, for instance, with regard to their refractive power, or to their behaviour with such bodies as do not effect their decomposition, their relative solubilities in ether, benzol, and so on, some slight varieties will be discovered between them, which will lead to a proof of their dissimilarity by experimental means.

If the compound ethers, which have been the subject of our consideration, in which all the hydrogen is replaced by chlorine, still possess the constitution of the original substances, it follows necessarily that the molecular arrangement of the atoms in the intermediate products must likewise be the same. The dichlorinated acetic ether, which is decomposed by water and potassa into acetic and hydrochloric acids, corresponds, therefore, in composition to the formula:

$(\text{C}_4 \left\{ \begin{smallmatrix} \text{H}_3 \\ \text{Cl}_3 \end{smallmatrix} \right\} \text{O} \cdot (\text{C}_2 \text{H}_3)^{\sim} \text{C}_2, \text{O}_3$ . Its conversion into these products is probably preceded, as with perchloracetic ether, by a separation of the two members, and as  $(\text{C}_4 \left\{ \begin{smallmatrix} \text{H}_3 \\ \text{Cl}_2 \end{smallmatrix} \right\} \text{O}$  cannot exist in the

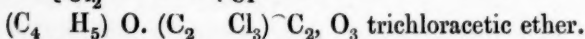
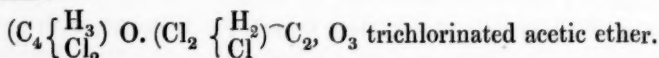
free state, by a transposition of these atoms to  $(\text{C}_2 \text{H}_3)^{\sim} \text{C}_2, \left\{ \begin{smallmatrix} \text{O} \\ \text{Cl}_2 \end{smallmatrix} \right\}$  (oxydichloride of acetyl). The trichlorinated acetate of oxide of ethyl, produced by a continuation of the process of substitution, is either acetate of oxide of trichlorethyl  $(\text{C}_2 \left\{ \begin{smallmatrix} \text{H}_2 \\ \text{Cl}_2 \end{smallmatrix} \right\} \text{O} \cdot (\text{C}_2 \text{H}_3)^{\sim} \text{C}_2, \text{O}_3$ , or

monochloracetate of oxide of dichlorethyl

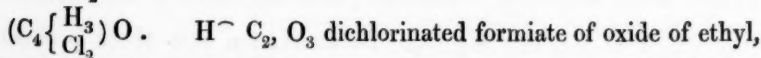
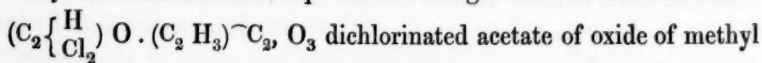


The deliquescent potassa-salt-containing chlorine, obtained therefrom according to Leblanc, by treatment with solution of potassa, is probably monochloracetate of potassa mixed with acetate of potassa; and the oily body simultaneously deposited, is possibly a secondary product of decomposition, produced from monochloracetic acid, in a manner similar to the formation of trichloride of formyl from trichloracetic acid.

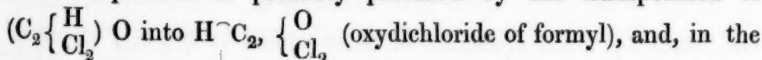
By the distillation of trichloracetic acid with alcohol containing sulphuric acid, as also by the treatment of dinoxychloride of trichloracetyl with alcohol, an ether isomeric with the above compound is produced, namely, trichloracetate of oxide of ethyl, differing greatly in its behaviour from the former, and particularly in the circumstance that it yields alcohol again, by treatment with boiling potassa. A comparison of their rational formulæ will suffice to account for their isomerism :



Among the intermediate substitution-products of compound ethers, in which only a portion of the hydrogen is replaced by chlorine, and which have, generally speaking, been less carefully studied, the dichlorinated acetate of oxide of methyl, and the dichlorinated formiate of oxide of ethyl are particularly distinguished, not merely by being isomeric, like the final products above-mentioned, but also by corresponding in their chemical comportment, without, however, being identical. If they be considered as composed according to the rational formulæ :



the decomposition of both by potassa into acetic, formic and hydrochloric acids, admits of a ready explanation. In the first compound, the decomposition is probably preceded by the transposition of



second case, by the metamorphosis of  $(C_4 \{ \overset{H_3}{Cl_2} \}) O$  into  $(C_2 \{ \overset{H_3}{H} \}) ^\frown C_2, \{ \overset{O}{Cl_2} \}$  (oxydichloride of acetyl). The formic acid is therefore produced, in the first case, from the basic member, and in the second case, from the acid member of the dichlorinated ethers; on the other hand, the

acetic acid produced in this reaction from the dichlorinated formiate of oxide of ethyl, must be considered as a product of decomposition of the member  $(C_4 \begin{Bmatrix} H^3 \\ Cl_2 \end{Bmatrix}) O$ , while it is pre-existing as such in the dichlorinated acetate of oxide of methyl.

*(To be concluded in the next Journal.)*

Dec. 16, 1850.

WILLIAM ALLAN MILLER, M.D., V.P., in the Chair.

Henry Medlock, Esq., and James Simpson, Esq., were elected Fellows of the Society.

The following Presents were announced :

"Journal of the Franklin Institute," Vol. XX. No. 4, October 1850; from the Society.

"Proceedings of the Philosophical Society of Glasgow," Vol. III. No. 4; from the Society.

"Recueil des Actes des Seances Publiques de l'Académie Impériale des Sciences de St. Pétersbourg, tenues le 28 Décembre, 1847, et le 19 Décembre, 1848."

XXXIII.—*Observations on the Constitution of the Alcohol-Radicals, and on the formation of Ethyl.*

BY B. C. BRODIE, F.R.S.

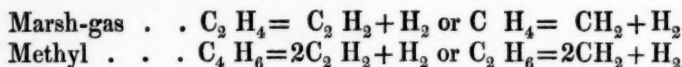
(SECRETARY OF THE CHEMICAL SOCIETY.)

On the occasion of the remarks of Dr. Hofmann on Dr. Frankland's second paper on the Organic Radicals, I made to the Society some observations on the theoretical constitution of those bodies. New facts have since been brought to light which strongly confirm the view which I then gave; and as the concluding remarks of Dr. Frankland's last paper have again brought this question before the Society, I take the opportunity of here making a memorandum of them.

Dr. Frankland pointed out various and, in my opinion, indisputable analogies between these hydrocarbons and hydrogen; and representing hydrochloric acid by the symbol HCl, the chloride of ethyl as  $C_4 H_5 Cl$ , and the isolated element hydrogen as H, he con-

sistently gave the formula  $C_4 H_5$  as that of the isolated ethyl. This formula, however, involved the singular anomaly that the atom of the gaseous ethyl occupied only half the space of the atom of all other hydrocarbons.

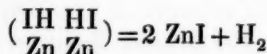
Gerhardt, with whose chemical ideas this anomaly was inconsistent, gave a theory of these bodies which doubled their formula.\* On his view, methyl was a homologue of marsh-gas. The constitution of the two substances being thus expressed :



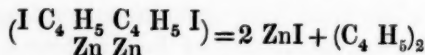
This view, however, not only doubled the formula of these bodies, but entirely set aside all their importance as radicals from the point of view of Frankland. Gerhardt considered himself further as justified in this by the absence of any remarkable chemical properties, by which these bodies were to be distinguished from other hydrocarbons.

Hofmann, in an elaborate, and indeed, most convincing argument, confirmed the necessity of doubling these formulæ; but at the same time he considered that the mode of the formation of the bodies appeared to be certainly in favour of the lower formula.† “Hydriodic acid and zinc,” says he, “yield iodide of zinc and hydrogen; in the same manner it would appear the iodide of an alcohol radical gives rise to the formation of iodide of zinc and the alcohol-radical.”

The perfect analogy of these reactions I admit; but I deny the inference as to the formula. If we represent the formation of the hydrogen  $Zn + IH = ZnI + H$ , we must, it is true, in consistency represent the formation of the radical ethyl in a similar manner,  $Zn + IC_4 H_5 = ZnI + C_4 H_5$ ; but the formation of the hydrogen may also be represented thus :



in which case the analogous formation of the ethyl is given by the expression :



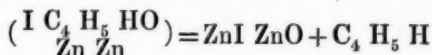
That this or some other similar expression which equally involves

\* Compt. Rend. Trav. Chim. 1849, 19, and 1850, 12.

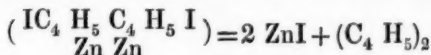
† Chem. Soc. Qu. J. III, 128.

the hypothesis that the formation of the isolated element is a chemical synthesis of the particles of the combined element, is the only rational expression of this reaction, is not an arbitrary assumption to meet the present case, but proved by a great variety of phenomena. I have elsewhere\* fully discussed that general law of chemical action, of which this is, I believe, but a particular example, and I shall confine my remarks now to the present instance.

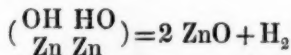
When zinc acts on the iodide of ethyl in the presence of water, the reaction, according to Frankland, is thus expressed :



this may be taken as the type of the other changes ; for substituting in the change, iodide of ethyl for water, we have the formation of ethyl



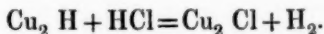
or substituting water for the iodide of ethyl, we have the formation of the hydrogen thus :



a reaction which truly takes place at high temperatures.

The view which I have given shows the relation between these phenomena, and that they are all expressions of one and the same law of chemical action, whereas, otherwise, at least two hypotheses and two different forms of chemical change are required to explain them. It is to me truly remarkable that Frankland, who maintains so strongly the analogy between the iodide of ethyl and water and the ethyl and hydrogen, yet denies the possibility of the substitution of these bodies for each other in this series of chemical changes.

There is a remarkable case of the formation of hydrogen to which I have referred in the paper before alluded to,† which I believe can only be accounted for on the view I have given. This is the decomposition of the hyduret of copper  $\text{Cu}_2 \text{ H}$  by hydrochloric acid. The substance itself and the reaction were discovered by Wurtz. Hydrochloric acid, which does not act upon copper, decomposes this body, thus :

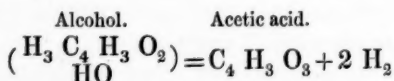


This I regard as (what is called) a simple case of double decompo-

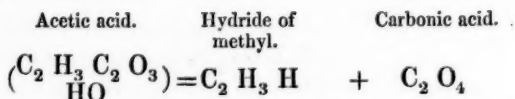
\* Phil. Trans. 1850, II, 789.

† Phil. Trans. 1850, II, 798.

sition. The formation of the hydrogen being the correlative fact to the formation of protochloride of copper. The oxidation of alcohols by hydrate of potash is likewise a case in point. The hydrogen in this experiment comes partly from the alcohol, and partly from the hydrate of the alkali, thus :

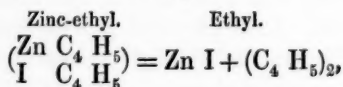


I regard the formation of the hydrogen as a chemical synthesis as truly as that of the acetic acid. The decomposition of water by the zinc-methyl is perfectly analogous to the formation of hydrogen by the decomposition of the hyduret of copper. Thus  $\text{Zn C}_2 \text{H}_3 + \text{HO} = \text{ZnO} + \text{C}_2 \text{H}_3 \text{H}$ , and in the oxidation of acetic acid by the hydrate of potash and the formation of marsh-gas or the hydride of methyl, the methyl combines with the hydrogen of the hydrate of potash in the same way as the hydrogen of the alcohol in the other experiment, thus :



we can therefore with one of these bodies effect the same kind of chemical changes as with the other.

These considerations induced me to try the experiment, whether the zinc-ethyl would not decompose the iodide of ethyl, with the formation of iodide of zinc and ethyl :



as the copper-hydrogen decomposes the hydrochloric acid with the formation of protochloride of copper and hydrogen. This experiment was wanting to complete the series of analogies, for, although Frankland\* had shown the presence of zinc-ethyl, or some body containing this compound, among the products of the reaction of zinc upon the iodide of ethyl, yet he had not shown that it took any part in the change; and, indeed, as it was a constant product of the decomposition, as also was olefiant gas and hydride of ethyl, when once formed, it might never be decomposed. With this view, I prepared a tube according to the directions of Frankland, containing

\* Chem. Soc. Qu. J. II, 298.

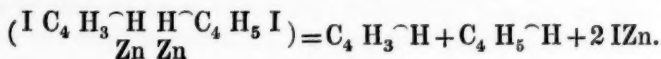


iodide of ethyl, with a great excess of zinc, and exposed it for some hours to a temperature of  $140^{\circ}$  to  $150^{\circ}$  C., at which temperature I had ascertained that a considerable proportion of zinc-ethyl was formed. I broke the end of the tube, allowed the gas formed to escape, and then introduced a fresh portion of iodide of ethyl, and re-sealed the capillary opening. The zinc was still in excess. The tube was now exposed for some hours to a temperature of  $100^{\circ}$  C. in a water-bath. On re-opening the tube, a certain quantity, although small, of gas was evolved, showing that action had evidently taken place. This might be the result of the action of the zinc-ethyl on the iodide of ethyl, but it was also possible that even at  $100^{\circ}$  the excess of zinc had acted on the iodide, for the residue still contained a large portion of zinc-ethyl, effervescing strongly with water; I now repeated this experiment, with the difference only that I at once placed the tube in the water bath. After several hours' action, the iodide of ethyl had disappeared, the zinc was covered with a crystalline crust, and on opening the tube under water, a small quantity of gas was given off, and the residue contained a large quantity of zinc-ethyl. Hence it is plain, that even at  $100^{\circ}$  zinc acts upon the iodide of ethyl. The question now was, whether the zinc-ethyl thus formed could be decomposed by the iodide at a higher temperature. My first experiments were quite unsuccessful: I took a small quantity of zinc and a very large quantity of the iodide of ethyl, and exposed the sealed tube for several hours to a temperature of  $100^{\circ}$ . It was then transferred unopened to an oil bath, and kept for several hours at a temperature of about  $160^{\circ}$  C. At the end of this time a much larger quantity of gas was given off than at  $100^{\circ}$ ; but the residue still effervesced strongly with water, nor could I at all succeed, even when very small portions of zinc were used, in entirely getting rid of the zinc-ethyl. The substance, however, which had been exposed to the higher temperature had undergone a great alteration in appearance, the tube being full of white crystals. The zinc-ethyl also, from the quantity of gas evolved, had been undoubtedly acted upon, although partially. It occurred to me that the reason of the cessation of the action, was that the zinc-ethyl, or other substance formed in the experiment, was not sufficiently soluble in the surrounding fluid, and that the action would be different in a different medium. Frankland\* had already found that the zinc-ethyl was soluble in ether; ether therefore appeared to be a suitable solvent. I therefore repeated these experiments, still with a great excess of the iodide of ethyl, but with the addition of

\* Chem. Soc. Qu. J. III, 293.

about twice its bulk of pure ether. The experiment succeeded perfectly. At  $100^{\circ}$  C., the zinc disappears, with the formation of only a trace of gas, and a large quantity of the zinc-ethyl. A small quantity of solid matter remains in the tube, but no zinc. A tube which had thus been exposed for several hours to  $100^{\circ}$  was now heated to  $170^{\circ}$  in an oil-bath. A large quantity of white crystals were deposited, and on opening the tube under water, a considerable quantity of gas was evolved, and the residue contained not a trace of zinc-ethyl, neither the fluid nor the solid matter effervescing with water. On ether alone, at this temperature, zinc has not the slightest action.

In the experiments of Frankland, there are two ways in which zinc decomposes the iodide of ethyl: the one in which the two particles of ethyl combine and ethyl is formed, the other in which one of these particles decomposes the other, with the formation of hydride of ethyl,  $C_4H_5H$ , and olefiant gas or the hydride of acetylene,  $C_4H_3H$ . This latter decomposition we may conceive to take place by the division of the hydrogen within the body, thus:



Frankland had indeed already ascertained the presence of ethyl in the gas produced by the action of zinc upon the iodide of ethyl and ether at a high temperature; but yet it seemed to me of importance to prove that the decomposition had not taken place entirely in this latter manner. For it was possible that the reaction of the zinc-ethyl on the iodide of ethyl might differ from that of the zinc, and that the constant formation of the hydride of ethyl and olefiant gas might be owing to this very reaction. I therefore dried the gas, and treated it with anhydrous sulphuric acid and manganese, after the method of Frankland, and conducted the experiment with the precautions which he recommends. After the necessary corrections for temperature and pressure, an experiment of this nature gave the following results: Total bulk of the gas, 39.78; gas after the absorption by  $SO_3$ , 33.54; gas after the absorption by alcohol, 4.53. This gives as the constitution of the gas, allowing the gas unabsorbed by sulphuric acid to be a mixture of ethyl and the hydride of ethyl:

Ethyl	. . . . .	6.24
Ethyl and hydride of ethyl	. . . . .	29.01
Nitrogen	. . . . .	4.53
		<hr/>
		39.78

It was plain, therefore, that only a very small portion of the iodide of ethyl had been decomposed in this other manner. In Frankland's experiment (without ether), the ratio of the gas absorbed by alcohol to the elayl was as 100:28·6; in this experiment it is as 100:21·5. Circumstances have as yet prevented me from completing the analysis of this gas; but this experiment, together with those of Frankland, I consider conclusive as to the nature of the reaction.

The next step in these experiments should be the decomposition of the iodide of methyl or of amyl by the zinc-ethyl, in which case, the formation of a compound hydrocarbon might be anticipated of the formula  $C_2 H_3$ ,  $C_4 H_5$ , or  $C_5 H_6$ .  $C_4 H_5$ , ethyl-methyl and ethyl-amyl.\* Ethyl stands to hydride of ethyl in the same relation as ether to alcohol, and would be to these hydrocarbons as ordinary ether to the compound ethers discovered by Williamson.† The parallel series being complete, thus:

H	H	Hydrogen	.	.	.	$\begin{matrix} H \\ H \end{matrix}$	} $O_2$ Water.
$C_4 H_5$	H	Hydride of ethyl	.	.	$C_4$	$\begin{matrix} H_5 \\ H \end{matrix}$	
$C_4 H_5$	$C_4 H_5$	Ethyl	.	.	.	$\begin{matrix} C_4 H_5 \\ C_4 H_5 \end{matrix}$	} $O_2$ Ether
$C_4 H_5$	$C_2 H_3$	Ethyl-methyl (unknown)			$C_4$	$\begin{matrix} H_5 \\ C_2 H_3 \end{matrix}$	
$C_4 H_5$	$C_{10} H_{11}$	Ethyl-amyl (unknown)			$C_4$	$\begin{matrix} H_5 \\ C_{10} H_{11} \end{matrix}$	} $O_2$ Amylate of ethyl.
					$C_2$	$\begin{matrix} H_3 \end{matrix}$	

\* Dr. Hofmann has communicated to me that he has actually tried this experiment with the iodide of amyl, but without success. The same causes, however, which prevent the reaction with iodide of ethyl, would here doubtless operate with yet greater force, the iodide of amyl being decomposed by zinc only with very great difficulty. It is probable that if the iodide of amyl were mixed with ether, the decomposition would be greatly facilitated. I can hardly doubt that, at any rate, the methyl-compound would be readily obtained.

† Phil. Mag. XXXVII, 350.

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J. J. GRIFFIN, ESQ.

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# INDEX.

## A.

- Abel, on the bichromate of ammonia, and some of its double salts, 199.
- Acetyl-urea, 90, 91, 98.
- Acid, alizaric, 249.
- amalic, 88.
- arsenious, action of, on albumen, 14.
- aspartic, formation of from bimate of ammonia, 187.
- azophosphoric, 143.
- — tabular view of the properties of, and of phosphoric and dentazophosphoric, 365.
- bisulphamylic, identity of, with hyposulphamylic acid, 158.
- bisulphethylic, identity of with hyposulphethylic acid, 18.
- bisulphimethylic, identity of, with hyposulphamethylic acid, 18.
- butyric, formation of succinic acid by oxidation of, 186.
- caproic, contributions towards the history of, 210.
- — decomposition of, under the influence of the galvanic current, 222.
- chloronaphthalic, 250.
- chrysianisic, 77.
- chromic, on the bichromate of ammonia, and some of its double salts, 199.
- cuminic, on the passage of, through the animal system, 181.
- dentazophosphoric, 354.
- dextroracemic, 81.
- hydrobromic, preparation of, 74.
- hydriodic, preparation of, 74.
- hydrocyanic, compound of bichloride of titanium with, 178.
- Acid hyposulphethylic, identity of, with bisulphethylic acid, 18.
- — preparation of, 20.
- — hyposulphamethylic, identity of, with bisulphimethylic acid, 18.
- — preparation of, 22.
- — hyposulphamylic, identity of, with bisulphamylic acid, 158.
- — levoracemic, 81.
- — metacetic, method of obtaining, in large quantities, 190.
- — nitrous, on the behaviour of aniline and the alcohol-bases with, 231.
- — cenanthylic, contributions towards the history of, 210.
- — decomposition of, under the influence of the galvanic current, 224.
- — pelargonic, researches on, 240.
- — racemic, 79, 82.
- — succinic, formation of, by oxidation of butyric acid, 186.
- — tartaric, 80, 81.
- — valeric, action of heat upon, 121.
- — xanthic, derivatives of, 84.
- Acids, on the separation of some of the acids of the series  $(CH)_nO_4$ , 82.
- — volatile, of the series  $(CH)_nO$ , physiological action of, 181.
- Albumen, action of arsenious acid on, 14.
- Alcohols, observations on the constitution of the alcohols and ethers, 45.
- Alcohol-bases, on the behaviour of aniline and the alcohol-bases with nitrous acid, 231.
- Alcohol-radicals, observations on the constitution of, and on the formation of ethyl, by B. C. Brodie, 405.
- — remarks upon the formulæ of, by A. W. Hofmann, 124.

- Alkaline carbonates, use of, for preventing incrustation in steam-boilers, 13.
- Alkaloids, artificial, the nitrogenated principles of vegetables considered as the sources of, 309.
- from beans, 305, 313, 314.
  - fern (*Pteris aquilina*), 315.
  - flax (*Linum usitatissimum*), 312.
  - guano, 314.
  - horse-flesh, 314.
  - lycopodium, 315.
  - peat, 313.
  - wheat (*Triticum hybernum*), 312.
  - wood, 313.
  - artificial, obtained by putrefaction, 314.
  - — by the acid of sulphuric acid, 314.
  - — relation of bases derived from aniline and ammonia with other groups of, 303.
- Alloy, natural, of silver and copper from Chili, 29.
- Amidogen-bases, 96.
- Amidogen-compounds of tungsten, 171.
- Amido-nitride of tungsten, 172.
- Ammonia, action of bromide of ethyl on, 299.
- action of, on chloroplatinate of ammonium, 176.
  - azophosphate of, 152.
  - dentazophosphate of, 360.
  - on the bichromate of, 199.
  - chrysanisate of, 77.
  - double compounds of bichromate of, with protochloride of mercury, 202.
  - formation of aspartic acid from bimalate of, 187.
  - relation of bases derived from aniline and ammonia with other groups of alkaloids, 303.
- Ammonia-meter, description of an, 206.
- Ammonio-azophosphate of iron, 152.
- Amyl, analysis and vapour-density of, 33.
- action of bromide of, on aniline, 297.
  - — amylaniline, 298.
  - — ethylaniline, 299.
  - boiling-point of, 34.
  - bisulphide of, 158.
  - caproate of, 213.
  - cyanate of, 95.
  - iodide of, 32.
  - isolation of, 32.
- Amyl-alcohol, physiological action of, 180.
- Amyl, hydruret of, 34, 41.
- Amylaniline, 298.
- action of bromide of ethyl on, 299.
- Amylethylaniline, 299.
- Amylethylophenylamine, 299.
- Amylophenamine, 96.
- Amylophenylamine, 297.
- Anderson, experiments on gases generated in a sewer, 13.
- use of alkaline carbonates for preventing incrustation in steam-boilers, 13.
- Aniline, on the behaviour of aniline and the alcohol-bases with nitrous acid, 231.
- , 96.
  - action of bromide of amyl on, 297.
  - action of bromide of ethyl on, 284.
  - action of bromide and iodide of methyl on, 295.
  - action of phenyl-alcohol on, 283.
  - relation of bases derived from aniline and ammonia with other groups of alkaloids, 303.
- Animal system, passage of cuminic acid through the, 181.
- Animal and vegetable kingdoms, observations on the adjustment between the, 52.
- Anisidine, 75.
- Anisol, 74.
- Anniversary Meeting, March 30, 1850, 97.
- Aromatic liquid, obtained by decomposing chlorophosphuret of nitrogen with alcohol, 362.
- Ashes of the cactus, composition of the, 57.
- Azophosphate of iron, 143.
- with ammonia, 146.
  - lead, 149.
  - mercury, 149.
  - potash, 151.
  - silver, 148.
  - alumina, 147.
  - ammonia, 152.
  - baryta, 149.
  - copper, 147.
- Azophosphates, composition of, 153.

## B.

- Baryta, action of heat on caproate of, 215.
- azophosphate of, 149.
  - dentazophosphate of, 360.
  - hyposulphamylate of, 159.

- Bases, relation of bases derived from aniline and ammonia with other groups of alkaloids, 303.  
 — researches regarding the molecular constitution of the volatile organic, 279.  
 — separation of, by diffusion, 266.  
 — synoptic view of basic compounds derived from ammonia, 308.
- Beans, alkaloids obtained from, 309, 313, 314.
- Bichloride of titanium, compound of, with hydrocyanic acid, 178.
- Bichloruretted salicylic ether, 78.
- Bichromate of ammonia, double compounds of, with protochloride of mercury, 202.
- Bimalate of ammonia, formation of aspartic acid from, 187.
- Binitranisidine, 76.
- Binitranisol, 74.
- Binitrophenetol, 78.
- Binitrosalicylic ether, 78.
- Bisulphide of amyl, preparation of, 158.  
 — preparation of the acid from, 159.
- Boilers, use of alkaline carbonates for preventing incrustation in steam-boilers, 13.
- Boiling-points, relation between chemical composition, boiling-points, and specific volumes, 104.
- Borate, on a native, 73.
- Boron, nitride of, 167.
- Brazier, contributions towards the history of caproic and cœnanthylic acids, 210.
- Brodie, observations on the constitution of the alcohol-radicals, and on the formation of ethyl, 405.
- Bromaniline, action of bromide of ethyl on, 292.
- Bromide of amyl, action of, on amylaniline, 298.  
 — action of, on aniline, 297.  
 — action of, on ethylaniline, 299.  
 — ethyl, action of, on amylaniline, 299.  
 — action of, on aniline, 284.  
 — action of, on ethylaniline, 287.  
 — methyl, action of, on aniline, 295.
- C.**
- Cactus, composition of the ashes of the, 57.
- Caffeine, 87.
- Cahours, on anisol and phenetol, 74.  
 — on the composition of mesitolole, 17.  
 — researches on pelargonic acid, 240.  
 — on the volatile oils obtained in the distillation of wood,
- Calvert, on the preparation of certain chlorates, and particularly of chlorate of potash, 106.
- Caproate of amyl, 213.  
 — baryta, action of heat on, 215.
- Caprone, action of nitric acid on, 220.  
 — composition of, 217.  
 — preparation of, 215.
- Caproyl, composition of, 226.
- Cast-iron, heat developed by friction of, 320.
- Cement, description of, for stopping the cavities of teeth, by T. J. Herapath, 367.
- Cetacea, creatine, a constituent of the flesh of the, 229.
- Chemical composition, relation between, and boiling-points and specific volumes, 104.
- Chemico-legal investigations, mode of precipitating all the metals contained in a liquid by one operation, in, 162.
- Chloraniline, action of bromide of ethyl on, 290.
- Chlorate of potash, preparation of, 106.
- Chloride of cyanogen and titanium, 177.  
 — action of, on toluidine, 154.
- Chlorine, action of, upon an equal volume of methyl,  
 — action of 2 vols. of, upon 1 vol. of methyl,
- Chlorophosphuret of nitrogen and its products of decomposition, by J. H. Gladstone, 135, 353.  
 — aromatic liquid obtained by the decomposition of, under the influence of alcohol, 362.  
 — composition of, 139.  
 — properties of, 138.
- Chloroplatinate of ammonium, action of ammonia on, 176.  
 — ethylamine, 95.  
 — methylamine, 94.
- Cholestrophane, 90.
- Chromate of copper and potash, 73.
- Chrysanisate of ammonia, 77.  
 — silver, 77.
- Chrysanisic ether, 78.
- Colouring matter, on the red colouring matters of madder, 243.  
 — of sugar, precipitation of, by a metallic oxide, 55.
- Copper, azophosphate of, 147.

- Copper, on a chromate of copper and potash, 73.  
 — in fuci, 71.  
 — natural alloy of silver and, from Chili, 29.  
 Crawhall, W., obituary notice of, 97.  
 Creatine, a constituent of the flesh of the cetacea, 229.  
 Cyanate of amyl, 95.  
 — ethyl, 90.  
 — methyl, 91.  
 Cyanogen, action of chloride of, upon toluidine, 154.  
 — chloride of, and titanium, 177.  
 Cyanogen-compound of titanium, 177.  
 Cyanurate of ethyl, 90.  
 — methyl, 90.

**D.**

- Danson, on the identity of bisulphamylic and hyposulphamylic acid, 158.  
 Debus, on the derivatives of xanthic acid, 84.  
 Dentazophosphate of ammonia, 360.  
 — of baryta, 359.  
 — of silver, 361.  
 Dessaignes, on the formation of aspartic acid from bimalate of ammonia, 187.  
 — on the formation of succinic acid by the oxidation of butyric acid, 186.  
 Dextroracemates and levoracemates, 81.  
 Diamylaniline, 298.  
 Diamylophenylamine, 298.  
 Diethylamine, 300.  
 Diethylammonia, 300.  
 Diethylaniline, 288.  
 — hydrobomate of, 288.  
 — action of bromide of ethyl on, 289.  
 Diethylophenylamine, 288.  
 Diffusion of liquids, 257.  
 — chloride of sodium, 259.  
 — various salts and other substances, 260.  
 — ammoniated salts of copper, 264.  
 — mixed salts, 265.  
 — salts of potash and ammonia, 271.  
 — hydrate of potash, 276.  
 — salts of soda, 277.  
 Diffusion, application of liquid diffusion to produce decomposition, 60.  
 — of one salt into the solution of another salt, 269.  
 — decomposition of salts by, 268.  
 — separation of bases by, 266.

- Distillation of wood, on the volatile oils obtained in the, 183.  
 Durocher, Malaguti and Sarzeaud, on the presence of lead, copper, and silver in sea-water, and on the existence of the latter in plants and animals, 68.

**E.**

- Eddoes, analysis of the ashes of the, 190.  
 Edwards, on the action of arsenious acid on albumen, 14.  
 Ether, observations on the constitution of the alcohols and ethers, 45.  
 — chrysanic, 78.  
 — salicylic, derivatives of, 78.  
 — bichloruretted salicylic, 78.  
 — binitrosalicylic, 78.  
 Etherification, observations on, by Prof. Graham, 24.  
 Ethyl, action of bromide of, on ammonia, 299.  
 — amylaniline, 299.  
 — aniline, 284.  
 — bromaniline, 292.  
 — chloraniline, 290.  
 — diethylaniline, 289.  
 — ethylaniline, 287.  
 — ethylochloraniline, 291.  
 — nitraniline, 293.  
 — action of solar light on the iodide of, 322.  
 — bioxysulphocarbonate of, 84.  
 — cyanate of, 90.  
 — cyanurate of, 90.  
 — observations on the formation of, by B. C. Brodie, 405.  
 — preparation of bisulphide of, 19.  
 Ethylamine, 96, 299.  
 — chloroplatinate of, 95.  
 — formation of, 92.  
 — preparation and properties of, 94.  
 — hydrochlorate of, 95.  
 Ethylammonia, 299.  
 Ethylamylophenamine, 96.  
 Ethylaniline, 285.  
 — action of bromide of amyl on, 299.  
 — action of bromide of ethyl on, 287.  
 — action of iodide of methyl on, 296.  
 — hydrobromate of, 286.  
 — platinum-salt of, 286.  
 Ethyl-cyamethane, 92.  
 Ethylobromaniline, 292.  
 Ethylochloraniline, 291.  
 Ethylnitraniline, 292.

Ethylonitrophenylamine, 292.  
 Ethylphenamine, 96.  
 Ethylphenylamine, 285.  
 Ethyl-oxamide, 95.

**F.**

Feculencies, sugar-, analysis of, by T. J. Herapath, 367.  
 Fern, alkaloids obtained from, 315.  
 Fibrine of muscular flesh, 188.  
 Field, on the composition of the ashes of the cactus, 57.  
 — on a natural alloy of silver and copper, from Chili, 29.  
 Flax, alkaloids obtained from, 312.  
 Flesh, on the fibrine of muscular, 118.  
 Formylamine, identical with methylamine, 89.  
 Frankland, researches on the organic radicals: Part II, amyl, 30.  
 — researches on the organic radicals: Part III, on the action of solar light upon iodide of ethyl.  
 Friction, heat developed by, of water, 319.  
 — mercury, 320.  
 — cast-iron, 320.  
 Fuci, lead and copper in, 70.  
 — silver in, 70.

**G.**

Gaultier de Claubry, on a mode of precipitating all the metals contained in a liquid by one operation (in chemico-legal investigations), 162.  
 Gerhardt and Laurent, on the action of ammonia on chloroplatinate of ammonium, 176.  
 Gladstone, on chlorophosphuret of nitrogen, and its products of decomposition, 135, 353.  
 — action of sulphur on the pentachloride of phosphorus, 5.  
 Graham, on the application of liquid diffusion to produce decomposition, 60.  
 — on the diffusion of liquids, 257.  
 — observations on etherification, 24.  
 Griffin, description of an ammoniometer, 206.  
 Gossleth and Brazier, contributions towards the history of caproic and cenanthylic acids, 210.  
 Guano, alkaloids obtained from, 314.

**H.**

Heat developed by friction of water, 319.  
 — mercury, 320.  
 — cast-iron, 320.  
 — on the mechanical equivalent of, 316.  
 Herapath, T. J., analysis of the ashes of the Spanish potato, and of the eddoes, 193.  
 — analysis of sugar-feculencies, 367.  
 — on a cement for stopping the cavities of teeth, 367.  
 Hofmann, on amidogen-, imidogen-, and nitrile-bases, 96.  
 — note on the action of heat upon valeric acid, with some remarks on the formulæ of the alcohol-radicals, 121.  
 — on the passage of cuminic acid through the animal system, 181.  
 — researches on the volatile organic bases, No. VIII. on the behaviour of aniline and the alcohol-bases with nitrous acid, 231.  
 — researches regarding the molecular constitution of the volatile organic bases, 279.  
 Horse-flesh, alkaloids obtained from, 314.  
 Hydrobromate of diethylaniline, 288.  
 — ethylaniline, 286.  
 Hydrocarbon, on propylene, a new hydrocarbon of the series  $C_n H_n$ , 111.  
 Hydrochlorate of ethylamine, 95.  
 — methylamine, 94.  
 Hydrosulphate of ammonia, action of, on mononitranisol, binitranisol and trinitranisol, 75.  
 Hydrurets, probable existence of the hydrurets of organic radicals in coal-gas, 42.  
 Hyposulphamylate of baryta, 159.

**I.**

Imidogen-bases, 96.  
 Iodide of ethyl, action of solar light upon, 322.  
 — methyl, action of, on aniline, 295.  
 — on ethylaniline, 296.  
 Iron, cast, heat developed by friction of, 320.  
 — ammonio-azophosphate of, 361.  
 — azophosphate of, 143.



**J.**

Joule, on the mechanical equivalent of heat, 316.

**K.**

Keller, F., method of obtaining metacetic acid in large quantities, 190.

Knop, on a chromate of copper and potash, 73.

Kolbe, on the chemical constitution and nature of the organic radicals, 369.

Kopp, on the relations between chemical composition, boiling-points and specific volumes, 104.

**L.**

Laurent and Gerhardt, on the action of ammonia on chloroplatinate of ammonium, 176.

Lead, azophosphate, 149.

— in fuci, 70.

Liebig, on the fibrine of muscular flesh, 188.

— on the separation of some of the acids of the series  $(C H)_n O_n$ , 82.

Light, on the action of solar, upon iodide of ethyl, 322.

Lime, on potasso-gypsite, a double sulphate of potash and, by J. A. Phillips, 348.

Liquids, diffusion of, 257.

Liquid diffusion, application of, to produce decomposition, 60.

Löwel H., on the supersaturation of saline solutions, 164.

Lycopodium, alkaloids obtained from, 305.

**M.**

Madder, on the red colouring matters of, 243.

Malaguti, Durocher, and Sarzeaud, on the presence of lead, copper, and silver in sea-water, and on the existence of the latter in plants and animals, 68.

Mène, on the preparation of hydrobromic and hydriodic acids, 74.

Mercury, heat developed by friction of, 320.

— azophosphate of, 149.

Mercury, double compounds of bichromate of ammonia with protochloride of, 220.

Mesitolole, 185.

— composition and vapour-density of, 17.

Metacetyl-urea, 91, 93.

Methyl, cyanate of, 91.

— cyanurate of, 90.

— action of chlorine upon an equal volume of.

— action of 2 vols. of chlorine upon 1 vol. of.

— action of bromide of, on aniline, 295.

— action of iodide of, on aniline, 295.

— ethylaniline, 296.

Methyl-alcohol, physiological action of, 180.

Methylamine, formation of, 92.

— obtained from caffeine, 89.

— chloroplatinate of, 94.

— hydrochlorate of, 94.

Methylaniline, 295.

Methylethylaniline, 296.

Methylethylophenylamine, 296.

Methyl-cyamethane, 92.

Methylophenylamine, 295.

Metals, on a mode of precipitating all the metals contained in a liquid, by one operation (in chemico-legal investigations), 162.

Metoluidine, preparation and analysis of, 155.

— and bichloride of platinum, 157.

Mitchell, analysis of deep well-water, from Messrs. Holt's brewery, Ratcliffe, 1.

Mononitranisol, 74.

Mononitroxylol, 184.

Moody, Col., obituary notice of, 98.

Muscular flesh, on the fibrine of, 188.

Muspratt, on the identity of bisulph-ethylic with hyposulphethylic acid, and of bisulphimethylic with hyposulphamethylic acid, 18.

**N.**

Nitraniline, action of bromide of ethyl on, 293.

Nitranisidine, 75.

Nitride of boron, 167.

Nitrile-bases, 96.

Nitrobenzanisidide, 76.

Nitrocinnanisidide, 76.

Nitrogen, chlorophosphuret of, 135, 353.

Nitrogenated principles of vegetables considered as the sources of artificial alkaloids, 309.

Nitrophenitidine, 79.  
Nitrotoluidine, 184.

## O.

Obituary notice of W. Crawhall, Esq., 98.  
—Colonel Moody, 98.  
Oils, volatile, obtained in the distillation of wood, 183.  
Organic bases, researches on the volatile, No. VIII. on the behaviour of aniline and the alcohol-bases with nitrous acid, 231.  
— researches regarding the molecular constitution of the volatile, 279.  
— researches on the, Part II., amyl, 30.  
— radicals, researches on the, by E. Frankland, Part III., on the action of solar light upon iodide of ethyl, 322.  
— radicals, on the chemical constitution and nature of, by H. Kolbe 369.  
Oxyamido-nitride of tungsten, 174.

## P.

Pasteur, on the characteristic properties of the two acids which compose racemic acid, 79.  
Peat, alkaloids obtained from, 313.  
Pelargyl, chloride of, 241.  
Pelargone, 242.  
Phenamine, 96.  
Phenetole, 78.  
Phenyl-alcohol, action of, on aniline, 283.  
Phillips, J. A., on potasso-gypsite, a double sulphate of potash and lime, 348.  
Phosphorus, sulphoperchloride of, 6, 11.  
Physiological action of analogously constituted chemical compounds, 179.  
Platinum-salt of ethylaniline, 286.  
Potash, azophosphate of, 151.  
— chlorate, preparation of, 106.  
— on a chromate of copper and, 73.  
Potasso-gypsite, a double sulphate of potash and lime, by J. A. Phillips, 348.  
Potato, analysis of the ashes of the Spanish, 193.  
Price, on creatine, as a constituent of the flesh of the cetacea, 229.

Propylene, a new hydrocarbon of the series  $C_n H_n$ , 111.  
— bromine-compound of, 115.  
— chlorine-compound of, 119.  
— preparation of, 115.  
Purpurine, 255.  
Putrefaction, alkaloids obtained by, 314.

## Q.

Quinine, action of certain reagents upon, 191.

## R.

Racemates, 82.  
Racemate of soda and ammonia, 80.  
Radicals, alcohol-, remarks upon the formulæ of, by A. W. Hofmann, 124.  
— observations on the constitution of the, and on the formation of ethyl, by B. C. Brodie, 405.  
— researches on the organic, by E. Frankland, Part II., amyl, 30.  
— researches on the organic, by E. Frankland, Part III. on the action of solar light upon iodide of ethyl, 322.  
— on the chemical constitution and nature of the organic-, by H. Kolbe, 369.  
Reynolds, J. W., on propylene, a new hydrocarbon of the series  $C_n H_n$ , 111.  
Report, Annual, of the Council, 97.  
— Treasurer's, 103.  
Richmond, on the bichromate of ammonia and some of its double salts.  
Rochleder, on caffeine, 87.

## S.

Salicylic ether, derivatives of, 78.  
Salts, decomposition of, by diffusion, 268.  
Salt, silver in sea-, 69.  
Sarzeaud, Malaguti and Durocher, on the presence of lead, copper and silver in sea-water, and on the existence of the latter in plants and animals, 68.  
Scanlan, experiments on gases generated in a sewer, 13.  
Schlossberger, on the physiological action of analogously constituted chemical compounds, 179.  
Sewer, experiments on gases generated in a sewer, 13.  
Silver, azophosphate of, 148.  
— chrysanisate of, 77.  
— in fuci, 70.  
— in land-plants and in animals, 70

- Silver in sea-salt, 69.  
 — in sea-water, 69.  
 — natural alloy of, and copper, from Chili, 29.  
 — tricyanurate of, 87.  
 Solutions, saline, on the supersaturation of, 164.  
 Stenhouse, on the nitrogenated principles of vegetables, as the sources of artificial alkaloids, 309.  
 Strecker, on the red colouring matters of madder, 243.  
 Sugar, precipitation of the colouring matter of, by a metallic oxide, 55.  
 — feculencies, analysis of, by T. J. Herapath, 367.  
 Sulphate, on potassa-gypsum a double, of potash and lime, by J. Phillips, 348.  
 Sulphanisolate, 78.  
 Sulphate, on potassa-gypsum, a double sulphate of potash and lime.  
 Sulphur, action of, on the pentachloride of phosphorus, 5.

**T.**

- Teeth, description of cement for stopping the cavities of, by T. J. Herapath, 367.  
 Titanium, chloride of cyanogen and, 177.  
 — compound of bichloride of, with hydrocyanic acid, 178.  
 — on the cyanogen compounds of, 177.  
 Toluidine, action of chloride of cyanogen on, 154.  
 — preparation of, 154.  
 Toluol, 184.  
 Tricthylamine, 96, 301.  
 Trinitranisol, 74.  
 Tungsten, amido-nitride of, 172.  
 — on the amidogen-compounds of, 171.  
 — oxyamido-nitride of, 174.

**U.**

- Ulex, on a native borate, 73.

**V.**

- Valeramine, chloroplatinate of, 96.  
 — formation and preparation of, 95.

- Valeramine, hydrochlorate of, 96.  
 Valerene, 44.  
 Vegetables, nitrogenated principles of, considered as the sources of artificial alkaloids, 309.  
 Vogel, Dr., Jun., on the action of certain reagents upon quinine, 191.  
 Volatile oils, obtained in the distillation of wood, 183.  
 Volumes specific, relation between chemical composition and boiling-points and, 104.

**W.**

- Warburton, on the precipitation of the colouring matter of sugar by a metallic oxide, 55.  
 Warington, notice of observations on the adjustment between the animal and vegetable kingdoms, by which the vital functions of both are permanently maintained, 52.  
 Water, analysis of deep well-, from Messrs. Holt's Brewery, Ratcliffe, by J. Mitchell, 1.  
 — heat developed by friction of, 319.  
 — on the presence of lead, copper and silver in sea-water, 68.  
 Wheat, alkaloids obtained from, 312.  
 Wilson, action of chloride of cyanogen, upon toluidine, 154.  
 Wöhler, on the amidogen-compounds of tungsten, 171.  
 — on the cyanogen-compounds of titanium, 177.  
 — on the nitride of boron, 167.  
 Wood, alkaloids obtained from, 313.  
 — volatile oils obtained in the distillation of, 183.  
 Wurtz, on the compounds of cyanuric and cyanic acid with the oxides of ethyl, methyl and amyl, and on the products resulting therefrom, viz.: acetyl- and metacetyl-urea, and methylamine, ethylamine, and valeramine 90.

**X.**

- Xanthogenamide, 85.  
 Xylidine, 184.  
 Xylol, or xylene, 184.

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2

